SCIENCE
NEWS 51

SCIENCE
NEWS

EDITED BY ARCHIE AND NAN CLOW

51

FIFTY YEARS
OF LIQUID HELIUM

K. MENDELSSOHN

LAST year the University of Leiden celebrated the fiftieth anniversary of the first liquefaction of helium. The achievement was the crowning result of years of preparation and careful planning by Kamerlingh Onnes, the Director of the 'Natuurkundig Laboratorium', an institution which now bears his name. For a long time the *Leiden Communications*, a scientific journal published by the laboratory, remained the only source of information in the field of low temperature research. The Leiden Laboratory attracted scientists from all over the world, and they, usually in collaboration with the permanent staff, made use of the unique facilities in order to carry out a wide range of investigations. Measured by the standards of its time, the technical effort involved in helium liquefaction and the specialized experimental knowledge required were quite exceptional, and it took almost twenty years before other helium liquefaction plants were operated in Toronto and Berlin. Even then, the scale remained smaller than at Leiden, and only in recent years has the Kamerlingh Onnes Laboratory been paralleled in other parts of the world. (Inset 5.)

While even today low temperature work is carried out on such a large scale in only a very few laboratories, the total volume of research has become enormous. This is chiefly due to the introduction of a reciprocating cooling engine that will liquefy helium, starting from the temperature of liquid oxygen – which is readily available almost everywhere – or even from room temperature. This cooling engine was originally developed by Kapitza during his Cambridge days in the thirties, and was further perfected by Collins at the Massachusetts Institute of

Technology. After the war it was made commercially available in America by the Arthur D. Little Company, who by now have sold well over a hundred machines. Most of these have gone into laboratories where low temperature work is carried out as a side line, and this has led to an interesting change in emphasis.

In Kamerlingh Onnes' days, large and costly equipment and highly trained personnel had to be concentrated on the task of providing the experimenter with a litre of liquid helium, i.e., with a few hours of research time. Since the technical effort played such a large role in the work, it had to be considered an essential part of it. Now, with liquid helium so much more easily obtainable, it is often argued that low temperature physics, as such, has ceased to exist, and that the use of low temperatures has become merely an ancillary service in large laboratories. This attitude is particularly strong in America, where in a number of large laboratories the low temperature research teams have been disbanded. Instead, a technician who operates the commercial helium liquefier will supply liquid helium to those sections of the laboratory where it is required. The uses may range from solid state research to nuclear targets. There is much to be said for this system, but it has certain disadvantages which are now emerging. Unfortunately, in most cases this realization has come too late, i.e., at a time when the low temperature research groups have been broken up and the personnel is either dispersed or has moved into other fields of research.

The low temperature field

The physics of low temperatures is that domain where the thermal energy is reduced to the same order as, or even lower than, the zero point of energy. It thus presents unique conditions both for the design of experiments and for the handling of the physical problems. In order to appreciate these problems and to devise means for their investigation, teams of scientists are needed whose thinking is trained along these lines, and to whom the special problems of low temperature physics have become second nature. It is well to remember that the laws of

'classical' physics which are based on the behaviour of aggregate matter at room temperature are 'classical' because this temperature region is too high for the effects of the quantum laws to become noticeable. At ordinary temperatures energy is shared out equally over all the different kinds of possible motion that an atom can have with respect to its neighbours. This law of equipartition, as it is called, breaks down as the temperature is lowered, the onset of non-classical behaviour depending on the nature of the substance. However, except for the case of diamond, the deviations from classical behaviour all occur below room temperature. The most striking feature is the falling off of the specific heats, which, in 1906, was so brilliantly explained by Einstein as the effect of the quantization of energy.

Planck had formulated the quantum theory six years earlier, but until then his fundamental paper had attracted remarkably little interest. This was partly due to Planck's own attitude. At 42, with a solid background of classical physics, Planck did not take too enthusiastically to the concept of energy having structure. Rather than accept and champion his own revolutionary discovery of the quantum principle, he seemed anxious to reconcile it with the current ideas of classical physics, according to which energy was a structureless fluid, allowing arbitrary subdivision. The decrease, at low temperatures, of the specific heat, which at that time was being investigated by Nernst and his school, appeared quite inexplicable within the system of classical physics. Einstein's explanation of this remarkable and striking effect through the quantum theory focused general attention on Planck's new concept of the nature of energy, however, and at the same time it correlated energy quantization with the realm of low temperatures.

In the same year of 1906 Nernst formulated the third law of thermodynamics which soon was to become the guiding principle of all low temperature research. This theorem eventually emerged as the basic rule in the application of the quantum concept to aggregate matter, but this was not the way by which Nernst had arrived at his great discovery. Being a theoretical chemist, Nernst was trying to find a method by which chemical

equilibria could be predicted. The early twentieth century saw the rapid growth of the chemical industry which, however, at that time still proceeded on the basis of isolated discoveries and very empirical rules. With large sums being invested in chemical production plant, the scientific planning of production processes became of ever-growing importance. For instance, it was felt that the fixation of atmospheric nitrogen by chemical reaction with hydrogen could be achieved on an industrial scale, provided the equilibrium between the two gases and the reaction product, ammonia, was known for a sufficiently wide range of temperatures and pressures. Nernst's idea was to compare the properties of two or more substances at a given temperature and pressure not by a reaction between them but through the knowledge of what had happened to these substances in a kind of thermal life history. He was looking for a reference point at which all substances would be in some way equal and it was obvious that he should choose for this purpose the absolute zero of temperature. The existence of such an absolute zero had been postulated more than 250 years ago by Amontons, and, by the laws of a perfect gas, its position in the temperature scale had been fixed as $-273°$ C. Throughout its long history, absolute zero had been regarded as the zero point of energy and this was still its significance when Nernst became interested in it early in the century. By then, with the kinetic theory of heat well established, absolute zero appeared as a state of ultimate rest for all molecular motion. Nernst therefore started with the idea that absolute zero might be a good reference point because all substance had zero energy. It came as a considerable surprise, when, as the result of his researches he realized that it was not the energy but another quantity, the entropy, which at the absolute zero vanished for all substances. The entropy, which first was formulated as a fundamental property by Clausius, describes the degree of disorder in a substance. Thus it became clear that absolute zero is not, as had been assumed for so long, a state of complete cessation of motion but a state of perfect order.

In this way the theoretical search for chemical equilibria had shown up a number of curious features in the thermal aspects

of aggregate matter which are all related to the physical significance of absolute zero; the decrease in the specific heats, the importance of the order concept, and the fact that the internal energy of a substance does not vanish. It was this last result that appeared, at the time, most disconcerting and was regarded almost as a magical mystery. The mind trained in classical physics found it hard to concede that, even at absolute zero, the substance should retain part of its molecular motion and much speculation was devoted to the exact nature of this zero point energy. Today, when everyone accepts that the hydrogen atom has a ground state that is distinguished from the other energy states only by the fact that it is the lowest one, the concept of zero point energy does not seem quite so strange.

The importance of the order parameter, the quantization of energy, and the existence of a large degree of motion that is not thermally excited, these then are the basic principles by which low temperature physics is distinguished. They had just been established when Kamerlingh Onnes liquefied helium 50 years ago and they have provided a continually growing impetus for research ever since. Looking back on what has been achieved in half a century, it is tempting to make some forecasts of the directions in which this exciting field is likely to move. There exists, of course, a vast and widening field of fundamental research. Not even a rough survey of this can be attempted in a short article and we must confine ourselves to accounts of the new cooling methods which, in the near future, may lead to temperatures of less than a millionth degree above absolute zero. There are now, also, the first signs of technical applications of low temperatures, and it is likely that these may become quite important in the next few years.

COOLING

The successful liquefaction of helium closed the chapter of cooling by gas liquefaction that had been opened with the liquefaction of oxygen by Cailletet and Pictet in 1877. The lowest temperature that can conveniently be obtained by evaporating helium under reduced pressure is about $1°$ K, but temperatures

as low as 0·7° K have been reached by the application of very fast pumps. For long, ordinary helium had been regarded as the gas with the lowest critical data, but quite recently sufficiently large quantities (of the order of a few litres at n.t.p.) of the light isotope ^{3}He have become available for cryogenic use. ^{3}He is obtained from the decay of tritium which in turn is the product of nuclear reactions involving neutrons from a reactor. It is therefore inevitable that the cryogenic use of ^{3}He should have started in the Soviet Union and the United States. In both these countries simple devices have been used in which a small quantity of ^{3}He gas is condensed under pressure and by contact with ordinary liquid helium. The vapour pressure over the condensed ^{3}He is then reduced and temperatures as low as 0·3° K can be obtained. The work of the Russians has, so far, been somewhat in advance because Peshkov and his co-workers in Moscow have been operating a rather more elaborate cryostat in which ^{3}He is constantly circulated. The gas is first condensed in thermal contact with ordinary helium and the liquid ^{3}He is then dropped into an evaporator where it is constantly pumped off. The evaporated vapour is in turn condensed again, thereby going through a closed cycle of operations. The advantage of this ingenious method lies in the fact that the heat passed into the evaporator is only the specific heat of the liquid ^{3}He between 1° K and the lowest temperature. This heat is small in comparison with the heat of evaporation of the same mass of ^{3}He which is continuously pumped off. Thus, experiments that have to tolerate a relatively large heat influx can be carried out down to 0·35° K because this is compensated for by the evaporation of ^{3}He. There are quite a number of investigations, particularly those on ordinary helium, in which a strong influx of heat is unavoidable, and for these the cycling ^{3}He cryostat of the Peshkov type is likely to become the method of choice.

As the supply of ^{3}He becomes more plentiful its cryogenic uses are bound to increase and it is probable that it will replace the magnetic method (to be described later) for temperatures down to 0·3° K. Also it may modify the magnetic techniques used at present allowing for lower starting temperatures. In the

temperature region below 1° K, ³He is already being used as a thermometric substance since measurement of its vapour pressure is much simpler than the use of magnetic susceptibility thermometers as hitherto. (Inset 6.)

With the liquefaction of helium it became clear that further progress to lower temperatures would have to rely on some method that was quite different from the customary process of gas liquefaction, since no gases with lower critical data were known. At the same time it was frequently debated whether it would be worth while reaching still lower temperatures since, in accordance with the third law of thermodynamics, absolute zero itself is unattainable. Producing lower temperatures, and their interest for research are, however, by no means unconnected, and cannot be considered separately. This will become clear at once when we investigate the general requirements for a cooling method. Since cooling is generally synonymous with a lowering of entropy, the entropy of the coolant must be high at the starting temperature. In order to decrease it, the entropy must further depend markedly on some parameter, other than the temperature, that can be varied conveniently. These conditions can be illustrated on the case of gas liquefaction. First of all, a gas is a highly disordered aggregate and its entropy is high. Secondly, the entropy of the gas depends markedly on the volume occupied by it, and we can conveniently lower the entropy by compressing the gas. The decrease in entropy is balanced by the heat of compression. Once this is carried away and not permitted to return, expansion of the gas, doing work, will result in cooling. This process can be repeated until the gas liquefies.

Cooling by demagnetization

It took almost twenty years from the liquefaction of helium until a new cooling method was suggested. In 1926 Giauque and Debye independently proposed to obtain very low temperatures by adiabatic demagnetization of a paramagnetic salt. In such a salt the elementary magnets of the electron spins do not interact, even at 1° K, and thus present a disordered pattern,

pointing in all directions. Applications of a strong magnetic field results in an alignment of the spins which, like the compression of a gas, is accompanied by the development of heat (of magnetization). Provision is made for this heat to be carried away and not to return. Subsequent demagnetization will then result in a cooling of the salt. The degree of this cooling depends on the strength of the field and the nature of the salt, but temperatures of less than 10^{-3} °K have been obtained.

A good deal has been written about the technique of the magnetic method. It was first used 25 years ago and has by now become standard practice in a considerable number of laboratories. Most of the work so far has been concerned with the properties of the paramagnetic salts themselves, and this provides a ready answer to the question whether there is anything of interest to investigate in a new lower temperature range. We have seen that in order to obtain lower temperatures, a system must be available whose entropy is high at the start and will decrease as the cooling process operates. This means that something is happening at these low temperatures which requires investigation, at least in the coolant itself. Thus, as long as it is possible to obtain still lower temperatures, this possibility in itself carries a guarantee that interesting physical changes will take place. This safe prediction does not, of course, exclude the possibility that other interesting phenomena, which are quite distinct from the cooling process, may turn up in the new range.

Much the same argument can be applied to the question of measuring temperatures in a newly opened region. The cooling process must always depend on a variation of entropy with temperature and this change in the entropy can, in turn, be utilized for thermometric purposes. The quantity actually measured is usually not the specific heat but often a more convenient property of the substance as, in the case of the paramagnetic salts, the magnetic susceptibility.

In its simplest form the paramagnetic cooling method is a discontinuous one in which a sample of salt is once demagnetized and then allowed to warm up gradually to the starting temperature. Measurements on either the salt itself or on another sub-

stance, thermally attached to it, are taken as the warming up proceeds. From this it is clear that, in order to be useful for accurate observations, the warming up rate must be slow, and the establishment of thermal equilibrium within the specimen, fast. The first conditions can be achieved by minimizing the influx of heat, while the second will depend on the heat conduction within the specimen and the heat transfer between its component parts. A very large volume of work on these experimental problems has been carried out in the last twenty-five years and rates of heat influx as small as 1 erg/min. have been obtained. For a long time erratic, high warm-up rates were observed and it became clear that the heat entering the specimen did not flow in from outside the cryostat but was in some mysterious fashion generated within it. Its source was eventually traced to small mechanical oscillations which the specimen, usually suspended by nylon threads, carried out as the result of vibration in the laboratory. The dissipation of this minute vibrational energy by frictional damping in the strings is large enough to spoil the experiment. This example, which is one of many, shows that the unique physical conditions obtaining at low temperatures require a very specialized experimental approach which is hardly to be found in a laboratory where cryogenics is merely an ancillary service.

In order to reach very low temperatures by single stage demagnetization a low starting temperature and a high magnetic field are required. Both these conditions require complex and expensive equipment, and it has been found advantageous to carry out the demagnetization in two stages. Apart from the saving in large pumps and magnets, this separation into two stages also allows a choice of two different salts for the higher and the lower end of the cooling range. The feasibility of multistage cooling depends on the making and breaking of thermal contacts between different parts of the apparatus. At higher temperatures this is usually achieved by gas conduction, but such a procedure is, of course, impossible below $1°$ K. For a number of reasons, mechanical contact devices also present very considerable difficulties. On the other hand, the heat conductivity of a metal wire, e.g., lead, is very much lower in the superconductive

pointing in all directions. Applications of a strong magnetic field results in an alignment of the spins which, like the compression of a gas, is accompanied by the development of heat (of magnetization). Provision is made for this heat to be carried away and not to return. Subsequent demagnetization will then result in a cooling of the salt. The degree of this cooling depends on the strength of the field and the nature of the salt, but temperatures of less than 10^{-3} °K have been obtained.

A good deal has been written about the technique of the magnetic method. It was first used 25 years ago and has by now become standard practice in a considerable number of laboratories. Most of the work so far has been concerned with the properties of the paramagnetic salts themselves, and this provides a ready answer to the question whether there is anything of interest to investigate in a new lower temperature range. We have seen that in order to obtain lower temperatures, a system must be available whose entropy is high at the start and will decrease as the cooling process operates. This means that something is happening at these low temperatures which requires investigation, at least in the coolant itself. Thus, as long as it is possible to obtain still lower temperatures, this possibility in itself carries a guarantee that interesting physical changes will take place. This safe prediction does not, of course, exclude the possibility that other interesting phenomena, which are quite distinct from the cooling process, may turn up in the new range.

Much the same argument can be applied to the question of measuring temperatures in a newly opened region. The cooling process must always depend on a variation of entropy with temperature and this change in the entropy can, in turn, be utilized for thermometric purposes. The quantity actually measured is usually not the specific heat but often a more convenient property of the substance as, in the case of the paramagnetic salts, the magnetic susceptibility.

In its simplest form the paramagnetic cooling method is a discontinuous one in which a sample of salt is once demagnetized and then allowed to warm up gradually to the starting temperature. Measurements on either the salt itself or on another sub-

stance, thermally attached to it, are taken as the warming up proceeds. From this it is clear that, in order to be useful for accurate observations, the warming up rate must be slow, and the establishment of thermal equilibrium within the specimen, fast. The first conditions can be achieved by minimizing the influx of heat, while the second will depend on the heat conduction within the specimen and the heat transfer between its component parts. A very large volume of work on these experimental problems has been carried out in the last twenty-five years and rates of heat influx as small as 1 erg/min. have been obtained. For a long time erratic, high warm-up rates were observed and it became clear that the heat entering the specimen did not flow in from outside the cryostat but was in some mysterious fashion generated within it. Its source was eventually traced to small mechanical oscillations which the specimen, usually suspended by nylon threads, carried out as the result of vibration in the laboratory. The dissipation of this minute vibrational energy by frictional damping in the strings is large enough to spoil the experiment. This example, which is one of many, shows that the unique physical conditions obtaining at low temperatures require a very specialized experimental approach which is hardly to be found in a laboratory where cryogenics is merely an ancillary service.

In order to reach very low temperatures by single stage demagnetization a low starting temperature and a high magnetic field are required. Both these conditions require complex and expensive equipment, and it has been found advantageous to carry out the demagnetization in two stages. Apart from the saving in large pumps and magnets, this separation into two stages also allows a choice of two different salts for the higher and the lower end of the cooling range. The feasibility of multistage cooling depends on the making and breaking of thermal contacts between different parts of the apparatus. At higher temperatures this is usually achieved by gas conduction, but such a procedure is, of course, impossible below 1° K. For a number of reasons, mechanical contact devices also present very considerable difficulties. On the other hand, the heat conductivity of a metal wire, e.g., lead, is very much lower in the superconductive

than in the normal state. At these low temperatures, the super-conductive state is the stable one but normal conductivity can be restored by the application of a moderate magnetic field. Accordingly, a heat switch between different parts of the apparatus simply consists of a wire of superconductive material, e.g., lead, and a small electromagnet with which superconductivity can be destroyed. Figure 1 shows the application of such a
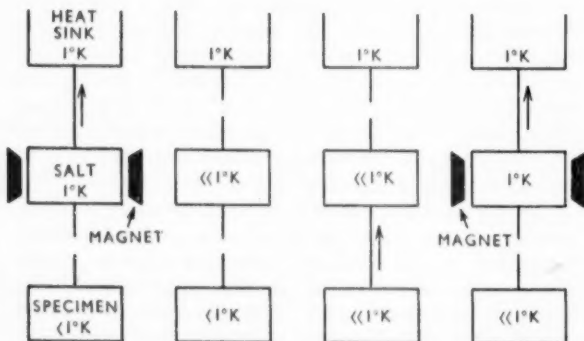

Fig. 1. Diagram illustrating the operation of Daunt's magnetic refrigerator. The arrows indicate the direction of the heat flow and a break in the connecting lines means that the thermal switch is superconductive.

device to a continuously working 'magnetic refrigerator'. Heat is withdrawn from the specimen to be investigated at the low temperature by a sample of paramagnetic salt which is alternatively magnetized and demagnetized. The superconductive thermal switches see to it that the heat from the specimen is transferred to the salt and then discarded into a heat sink at 1° K.

Nuclear demagnetization

In the same way as the cooling methods involving gases are ultimately limited by the gas turning into a liquid, so the electron

spin cooling devices must cease to operate when the spins become fully aligned. The interaction between the electron spins can be further decreased by diluting the salt, but then the cooling capacity is diminished. However, once the basic idea of magnetic cooling methods had been conceived, it was natural that other systems than that of the electron spins should be investigated. The obvious choice is that of the spins of the atomic nuclei, and nuclear demagnetization as a new cooling device, leading to very low temperatures, was suggested independently by Kurti and Simon and by Gorter. While the solution itself seems obvious, its realization is made difficult by very rigorous experimental requirements. The nuclear moments are roughly a thousand times smaller than the paramagnetic ones and therefore the gap between the two methods is rather too large to be bridged conveniently. For instance, at a temperature of 0·01° K a magnetic field of the order of 100,000 oersted is needed in order to achieve the necessary nuclear alignment for the subsequent cooling by demagnetization. Quite apart from the difficulty of producing fields of this magnitude – free from disturbing ripple – over a volume of, say, 20 cubic inches, the problem of establishing thermal equilibrium between the component parts of the apparatus at 0·01° K is formidable. (Insets 7 and 8.)

After preparatory research lasting several years, a first successful nuclear cooling was carried out in 1956 at Oxford, a few months before the death of Sir Francis Simon. He thus lived to see the success of the method for the realization of which he had worked so untiringly. In principle the experiment followed the pattern of multi-stage paramagnetic cooling. The nuclear cooling was preceded by an ordinary electron paramagnetic stage and the thermal connexion to the nuclear stage was made by a very great number (1,500) of fine copper wires. Their 'warm' ends were embedded in the paramagnetic salt at 0·01° K, heat contact being achieved by the large total boundary surface between salt and metal. The other end of the wires served directly as the nuclear stage. The copper nuclei were first aligned and then demagnetized, and a temperature of the order of 10^{-3} °K was reached. In this first experiment no heat switch between the

paramagnetic and the nuclear stage was used and the latter therefore warmed up fairly rapidly. It is clear that, as the method is being developed, efforts will be made to reduce the influx of heat into the nuclear stage and to maintain the very low temperature for a longer time.

Future trends

At the International Low Temperature Conference in Leiden, held in the summer of 1958 in celebration of the fiftieth anniversary of the liquefaction of helium, a more direct and possibly more far-reaching approach to absolute zero was mooted. Professor Kittel of the University of California suggested an ingenious method in which the entropy of the nuclear spins is to be removed at $1°$ K by saturating the electron spin resonance in a metal specimen with microwave power in a static magnetic field of only 10,000 oersted. He expects that removal of first the alternating and then the static field will result in temperature drops to 10^{-3} and $10^{-7}°$K respectively. If the forecast turns out to be correct, and if the experimental difficulties can be mastered, the new method will become very attractive, not only because the static magnetic field required is easily obtainable, but also because the metal serves as the working substance throughout, and no heat transfer problems will arise between the two stages of the process.

A very different method for obtaining equally low temperatures was proposed some eight years ago by Pomeranchuk in Russia. If it works, it may be much simpler than any of the magnetic methods, but its feasibility depends on some low temperature properties of ^{3}He that have as yet not been fully explored. Pomeranchuk's theoretical interpretation of the experimental data then available led him to postulate that at temperatures well below $1°$K the entropy of solid ^{3}He would become higher than that of the liquid. The reason for this inversion of the usual conditions is to be found in a spin alignment in the liquid phase, while in the solid the spins are to remain disordered down to $10^{-7}°$K. Accordingly, compression of liquid ^{3}He, below the inversion temperature of the entropy, until it becomes solid

should result in a cooling to 10^{-7} °K. The first part of Pomeranchuk's prediction came true in 1954 when W. Fairbank and others in America observed that spin alignment in the liquid becomes very noticeable below 0·5 °K. As for the second prediction, that is the retention of spin disorder in the solid state, the evidence so far available is insufficient and contradictory. Magnetic and calorimetric observations suggest that a change in the solid may occur already at 0·1° K, but whether this is the spin alignment expected by Pomeranchuk at 10^{-7} °K or is due to a crystal transformation is by no means clear. In the former case, the actual cooling on crystallization would only be small. However, it is to be expected that within one or two years we will know whether Pomeranchuk's simple method has hopes of success.

APPLICATIONS

Until the winter 1938–9 it seemed clear that nuclear physics would have few, if any applications. Predictions as to whether, and when, a field of basic research will lend itself to the solution of technical problems are, generally, impossible. The reasons, set out earlier in this article, why low temperature research has attracted so much attention are purely academic, and even Nernst's original approach to the prediction of chemical equilibria had, in the end, practically no influence on the way in which research programmes have been shaped. The study of quantum effects in aggregate matter has held the stage in the past fifty years.

The availability of oxygen in liquid form has, of course, led to a number of applications of which the liquefaction process in itself is by far the most important. Oxygen is used in a great number of chemical and metallurgical processes, and has lately come into great demand in steel making. The low temperature liquefaction, or more correctly fractionation, of air is now being used for extracting from the atmosphere oxygen in tonnage quantities. Storage, transport, and piping of liquid oxygen received early attention, and have by now been widely developed.

In recent years two other liquefied gases have attracted

considerable notice and their practical use is likely to become important in the near future. These are methane and hydrogen. Methane occurs as natural gas or as a by-product in oil refineries. It is important as a fuel, but up to now the cost of storage and transport in gaseous form have in many cases made its use uneconomical. Plans are now being actively pursued to liquefy large quantities of methane where it is available cheaply and then to ship it to the consumer in low temperature tankers. Its boiling point is 111° K so it is clear that the handling of it will be very different from transporting crude oil.

Liquid Hydrogen

In the fifty years that followed the liquefaction of hydrogen by Dewar in 1896, the liquid has only served in rather small quantities as a cryogenic agent for research. Owing to its inflammability and the attending risks of fire and explosion, its use has been limited, and its elimination from helium liquefaction was regarded as one of the chief merits of the reciprocation engines designed by Kapitza and Collins. However, the need for large quantities of deuterium for nuclear work has now focused attention on the low temperature distillation of hydrogen, and we may expect to see sizeable liquefaction and separation plants put up in the near future. A beginning in the handling of large quantities of liquid hydrogen has recently been made in the Cryogenic Engineering Laboratory of the National Bureau of Standards at Boulder, Colorado. There, two identical hydrogen liquefiers, each of 300 litres per hour capacity, have been constructed and operated. It is not impossible that liquid hydrogen may also become important as aviation or rocket fuel. It is not the best propellant so far as bulk is concerned, but its small weight may be found useful in some cases.

Experiments have also been carried out to employ liquid hydrogen as magnet coolant for the production of very high fields. Its latent heat is much smaller than that of liquid air, so hydrogen is inferior in its cooling capacity, but the electrical resistance of coils made of pure copper or aluminium becomes very small at 20° K, the boiling point of hydrogen, and the Joule

heating in them is much reduced. High magnetic fields will play a significant role in the establishment of controlled thermonuclear reactions, and this application of liquid hydrogen may therefore become important.

Loss-free electromagnetic devices

The idea of loss-free electromagnetic devices was immediately suggested when superconductivity was first discovered, and a number of efforts have since been made to find metals or alloys that would exhibit superconductivity at higher than helium temperatures. Today this difficulty does not appear as decisive as at the time of Kamerlingh Onnes. A compound, niobium nitride, NbN, has been found which becomes superconductive at the temperature of liquid hydrogen, and, rather more important, the liquefaction of helium can now be carried out quite easily. The real difficulty in the use of superconductors in magnetic devices is the fact that superconductivity is destroyed by fields of only a few hundred oersted. Higher fields can be tolerated in some alloys, or in thin superconductive films, but whether these will lend themselves to the production of high magnetic fields is still very much an open question. Superconductors have been employed as very sensitive bolometers for the detection of weak thermal radiation, but this use has sunk into insignificance in comparison with an entirely new application.

The Cryotron

The operation of a computer depends on circuit elements which, on receiving a signal, will make or break a current. A number of such elements have been used, of which the electronic valve is the best known. Speed and reliability in the switching process are essential features. It is now realized that superconductors offer possibilities that are so superior to other devices that they far outweigh the cost of the liquid helium required for maintaining the necessary low temperature. In its simplest form the 'cryotron', as the new element has been called, consists of a superconductive wire around which a single layer coil of another superconductor is wound (Figure 2). Conditions are arranged
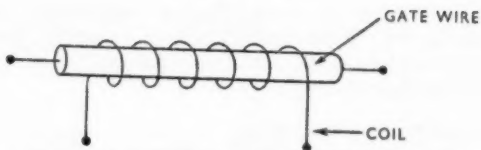
Fig. 2. Diagrammatic representation of a cryotron.

so that the coiled superconductor will tolerate higher fields than the 'gate' wire. When the coil is not energized, a current can run through the coil, which will itself remain superconductive and render the gate non-superconductive so that the metal regains its normal resistance. Since the change in the gate is from zero to a finite resistance, the rest of the circuit can be so dimensioned that it senses this change as the opening or closing of a contact. This is thus a relay with current gain. Apart from its simplicity, the individual cryotron element need not weigh more than a few milligrams and a thumb nail will provide space for a dozen of them. Moreover, the power dissipation of the device is negligible. While the cryotron offers outstanding performance in operation, superconductivity provides even more striking facilities for the other function of a computer, i.e., storage. In general a good memory device is more difficult to construct than a switching element, but here, too, a simple solution is provided. If a superconductive circuit is split into two branches, the currents in them are inversely proportional to the inductances. If one of the branch currents is interrupted, for instance by use of a cryotron switch, then the whole supercurrent is forced into the other branch. This state is maintained even when the cryotron gate is again made superconductive. The current in the circuit can now be regarded as being made up of the two original branch currents with a superimposed circulating current. If now the external current is switched off, the loop made up of the two branches is left with the persistent circulating current. The device has thus stored the memory of the current flowing through the branches when one of them was cut. The circuit will retain this stored information as long as it is not warmed

up, but it can, of course, be erased by applying fresh currents to cryotron switches in the branches, or by passing a big enough current to render both branches normally conducting (Figure 3).
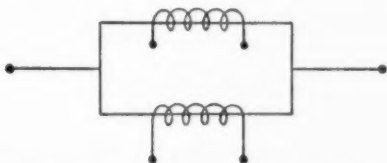

Fig. 3. A superconductive memory device. The cryotron switches in the branches are used to break the circuit.

These are just a few of many possible superconductive computer devices. By using suitable designs, switching times of a few millimicroseconds have been obtained, and there seems to be no doubt that the future will bring very compact, fast-working computers with large storage capacity made up of superconductive components. Apart from the more orthodox applications, these computers will be especially suitable for incorporation into missiles where they can perform the required calculations for guidance, orbiting, and so on, without having to rely on calculated results telemetered from the ground.

The applications of low temperatures mentioned here are only the more striking ones. The alignment of atomic nuclei by low temperature methods has led to the discovery that parity is not conserved in weak interactions. The use of liquid hydrogen as working substance in expansion chambers has led to important advances in nuclear physics. Thermal conductivity measurements on superconductors have led to a new and powerful metallurgical tool. Deposition of electrical discharge products at helium temperatures has permitted the trapping and subsequent investigation of free radicals.

In conclusion one can feel confident that the next fifty years of liquid helium will prove again the golden rule that effort and money devoted to basic research are well spent.

CACAO–ITS CULTIVATION, PROCESSING, CHEMISTRY

B. D. POWELL

COCOA and chocolate are manufactured from the fermented and dried cacao bean, the seed of the tropical tree *Theobroma cacao,* the fermentation and drying being carried out in the country of origin.

In 1957, 101,000 tons of beans, valued at £21,000,000 were imported into the United Kingdom, and the individual consumption of cocoa and chocolate confectionery was 12 lb, the highest in the world.

From these facts the importance of the cacao crop is clear, and in this article the history and use of cacao, its classification, botany, cultivation, pests and diseases, fermentation, drying, and chemistry will be discussed, and the manufacture of cocoa and chocolate outlined.

HISTORY

The cacao tree, indigenous to the Amazon and Orinoco forests of South America, was cultivated by the Mayas and Aztecs before Columbus discovered the New World, and it was he who, after his fourth voyage, introduced the cacao bean to Europe.

American Indians prepared a beverage, by whisking with water, dried and roasted cacao beans that had first been ground, and then mixed with corn and spices. Montezuma, the Emperor of the Aztecs, was fond of the drink and his daily consumption is alleged to have been 50 goblets; this fondness was evidently shared with the Swedish botanist Linnaeus, who, at a later date, 1720, named the tree bearing the bean *Theobroma cacao* (Food of the Gods).

The custom of drinking chocolate (different from both the

eating chocolate and the cocoa drink as we know them today) spread to England from Europe in the seventeenth century, and chocolate houses were opened for the sale of chocolate as a drink, and also as cakes from which the drink could be prepared in the home. Pepys wrote in 1664: 'To a coffee house to drink chocolate, very good!' In the eighteenth century the methods of grinding the imported beans were improved, but the beverage still remained much the same as the Aztec preparation in that no fat (cacao butter) was removed from the bean, though by this time it was usual to add sugar.

In 1828 van Houten removed some of the fat by pressing the roasted bean to produce the cocoa powder as we buy it at the present time. The extracted fat could then be mixed with sugar, and with roasted and ground beans, to give a true eating chocolate similar to that of today. A reduction in the price of cocoa was made possible thereby and the popularity of cocoa and of the new eating chocolate grew rapidly.

Another great advance was made in 1867 when Peters, in Switzerland, devised a method of manufacturing milk chocolate.

THEOBROMA SPECIES AND COMMERCIAL VARIETIES

Only two of some twenty species of the genus *Theobroma* described in the literature produce the cacao of commerce, *T. cacao* and *T. pentagona* (the latter in insignificant amount): the remainder are not cultivated.

There are several varieties of *T. cacao* which differ in the appearance of their pods and seeds, though the characteristics of their vegetative parts are similar. Three varieties of commercial cacao are generally recognized – Criollo, Forastero, and Trinitario.

When Criollo beans are removed from the pod (which shows ten deep longitudinal furrows) and cut through, the cross-section exposed is white or pale purple in colour, becoming light cinnamon brown after fermentation and drying. Few countries now grow pure Criollo – Venezuela and Ceylon are examples of those that do – and the annual world production has decreased over the past fifty years until it is now in the region of 5,000

tons. The flavour of the chocolate from Criollo beans is distinctive, though not strong, and is sought by some manufacturers.

Forastero beans have a deep purple 'cut' when unfermented, and after fermentation are chocolate brown. The pod, too, is different – the husk is thicker and more lightly furrowed. Forastero cacao is found in almost all cacao areas and since it grows more readily than Criollo, and is less exacting in its demands, has partly replaced it in many countries. Annual production is over 700,000 tons, mostly from West Africa and Brazil. The variety is described more closely as Forastero Amelonado.

Production of the third type of cacao, Trinitario, stands at about 50,000 tons, mostly from the West Indies and Central America; it is harvested from trees that are Criollo-Forastero hybrids. Trinitario and Criollo together comprise the so-called 'choice cacaos' and command a premium over Forastero Amelonado.

The total annual world production, though it fluctuates from one year to another, now runs at about 800,000 tons, and Table I shows its growth since the end of the last century.

TABLE I
Cacao production 1895–1955

Year	Tonnage	Percentage choice cacao (approx.)
1895	75,718	–
1905	143,587	–
1915	291,712	40
1925	487,660	–
1935	667,431	–
1945	614,000	–
1955	800,000	7

During the period under review the quantity of 'choice' cacao has decreased, both absolutely, and relatively to the total crop. The greatest contribution to the overall expansion has been the planting of Forastero Amelonado cacao in West Africa and Brazil.

THE CACAO TREE

Botany

The cacao tree (Inset 1) takes about ten years to grow to its full height of 20 to 30 ft though it is common plantation practice to prune, with a consequent reduction in height, the object being to make the harvesting of the pods easier. The mode of branching is uncommon – after growing for 3 to 5 ft, the straight stem forks and gives rise to fan branches which are almost horizontal, a phenomenon known as jorquetting. Later, a chupon or sucker arises below the jorquette, and after growing for a few feet vertically, the forking occurs once more, and usually another once or twice in the life of the tree. On the fan branches the leaves are alternate and lie in a horizontal plane, while those on the chupons and the original main stem of the seedling are borne in a 3/8 spiral. The young leaves of the tree are limp, hang vertically and are of a light green or red colour, but when mature become stiff, leathery, and evergreen with a length of up to 15 inches. Another unusual feature of the tree is that it bears flowers and pods on the main stem and the older branches.

Pollination in relation to the cacao tree has been little studied until recently, presumably because it has never been a limiting factor in cocoa production. Although several thousands of flowers may appear on a tree during the course of a year, percentage pollinated is low, perhaps only 10–40 per cent of the total. Only a small proportion of the pollinated flowers come to fruition and a smaller number still become mature pods. The limiting factor is the wilting of the immature pod, known as a cherelle. Work in Ghana has shown that pollination is due to flying insects, and in particular to the Heleid midges, which have also been reported in other cacao-growing countries. The large-scale use of insecticides for spraying against capsids, and as a possible means of controlling the ants that attend mealybugs (the vectors of the swollen shoot viruses) makes it important to investigate their effect on the midge, lest the stage be reached when pollination is adversely affected.

Ripening of the pod takes about 18 weeks. When ripe it weighs

approximately 1 lb and contains within its husk some 30–40 beans arranged around the central placenta and surrounded, individually, by a mucilaginous pulp. The colour of the healthy mature pod depends on the variety of the tree, and may be red, through a range of intermediate shades, to yellow. A tree will bear when 3–10 years old, the age being dependent largely on the variety. The yield increases during the first 25 years and then remains more or less constant for a like period of time. For a tree the figure of merit is the pod index – the number of pods from which 1 lb of dry fermented beans can be obtained – usually in the region of 12 for West African Amelonado.

Cultivation

The cacao tree grows in hot, humid conditions and is found between 20° N and 20° S latitude, and then mainly between 10° N and 10° S – in fact, it prefers the climatic conditions of the tropical rain forest zone. It is cultivated in areas that have average annual rainfall figures as widely different as 45 and 200 inches. Temperature is not too critical, but ideally the day minimum in shade conditions should be 80° F. An increase in altitude has an adverse effect only in that is usually leads to a reduction in temperature. The cropping season is well defined in some countries, for instance in Nigeria and Ghana, but in others the harvest is spread more or less uniformly over the whole year.

It is customary to establish young cacao trees under a ground shade of plants such as maize or plantains, and to provide a permanent shade of large trees. This question of permanent shade is many sided, though it is generally agreed that it is beneficial if the shade provided is not excessive.

Soils for cacao growing must possess the necessary nutrients for the growth of the tree and also contain air and water in sufficient amount throughout the year. The aeration and water relationships of the soil are perhaps the more important factors since the nutrient status can be modified fairly easily by the addition of fertilizers. Attempts are now being made to increase the amount of information available on the mineral needs of cacao trees.

Pests and diseases

Growing cacao suffers from a number of diseases and pests, some of which are of local, and others of widespread, occurrence. Amongst those of major importance are swollen shoot (a virus disease), black pod, witches' broom, and monilia (fungus diseases), and insect attack by capsids.

Swollen shoot was recognized as a virus disease in 1938, some three years after it had become serious in Ghana, though the earliest outbreaks now seem to have occurred in that country 25 years previously. Hitherto, the symptoms – swelling of the shoots and branches, and characteristic mosaic patterns on the leaves, followed by death of the tree – had been attributed variously to poor soil, insufficient shade, and drought. Over 20 virus strains of differing virulence have been isolated and the disease is known in Ivory Coast, Ghana, Nigeria, and in a mild form in Trinidad as well.

Cacao viruses are spread by mealybugs (carried by the wind or ants) which become infective after several hours of feeding, remaining so for some hours afterwards. Transmission of the virus takes only a few minutes. Exposed mealybugs are readily killed by several insecticides, but the protection given by the 'tents', which the attendant ants form, made spraying useless as a control measure.

Formicides now under test may prove effective against the ants, and indirectly, therefore, against the disease. Investigation of systemic insecticides as a control measure against mealybugs has not given encouraging results – a preparation is painted on the trunk or leaves, placed in the ground near the roots, or injected into the tree direct – to make the tree poisonous to the feeding insect. Selection of resistant types of tree has been made and this offers perhaps the best long term solution : in the short term, the cutting-out (65 million trees in Ghana and Nigeria) of infected trees, followed by burning and replanting, has been resorted to, a method that had serious political repercussions in Ghana a few years ago. Fortunately, the continued practice of this measure has led to the disease now being 'contained'.

Black pod is a serious disease, found universally in cacao areas, which attacks pods in wet conditions and is due to the fungus *Phytopthora palmivora*. Its incidence is higher when the annual rainfall is heavy and the humidity high, conditions that lead to rapid spread of the fungus from pod to pod and tree to tree. The pod turns brown around the site of the attack and the discoloration spreads quickly over the entire pod which then goes rotten. Bordeaux mixture has proved the most effective fungicide. If the pods are mature at the time of attack the beans within may still be in a suitable condition for fermentation.

In South America, both witches' broom and monilia have also proved to be harmful fungus diseases. The former attacks all the living tissues, and only by breeding resistant trees is control being achieved : the latter causes pod rot and can be dealt with by spraying with Bordeaux mixture.

Much damage is caused by capsid bugs in many cacao-growing countries. The insects inject a toxin into the tissues while feeding and the capsid wounds are frequently invaded by a fungus. Dieback, or even death, results particularly if the tree is weakened by drought or repeated attack. Insecticides such as D.D.T. and B.H.C. have proved effective against capsids.

THE CACAO BEAN

Fermentation

Fermentation of cacao beans, begun within one or two days of harvesting the pods, is the first, and one of the most important, processes, involved in the production of cocoa and chocolate. After fermentation the beans are dried, when certain chemical changes which began in fermentation are continued and others come into play.

The more accessible pods are removed by cutting through the stalk with a knife, and since the tree will not bear climbing, the more remote are dislodged with a picker which consists of a curved blade on the end of a long pole.

The pod (Inset 2) is opened by knocking it against a large stone, or another pod, or by splitting the husk with a cutlass; this last method, though frequently used, is to be deplored,

because the beans can be damaged with a risk of insect entry and infestation later. A wooden spoon is an aid to the removal of the beans from the pod, separating them also from the placenta and any broken pieces of husk.

Cacao beans are fermented in many different ways – in holes in the ground, in heaps, baskets, or boxes: even old wine barrels are used in Ivory Coast. The period of fermentation is from 6 to 8 days for Forastero beans, and rather less for Criollo, with occasional mixing. Variations in method and duration are so great that it would be difficult to find two quite identical procedures. In the first day of fermentation, some of the pulp runs away as 'sweatings' and the temperature begins to rise gradually (Table II) until by the third day, the bulk is at its maximum* of about 45° C, where it is maintained until the beans are put to dry, either in the sun, or in an artificial dryer.

TABLE II. *Temperature and acidity changes in a fermenting box*

Days	0	1	2	3	4	5	6
Temperature °C	28	33	38	44	43	44	42
Cotyledon pH	6·6	6·2	5·5	4·7	4·8	4·9	5·0
Pulp pH	3·7	3·8	3·8	4·0	4·8	4·9	5·0

pH of cotyledon at end of sun drying (13 days after beginning of fermentation) 5·3

When fermentation and drying have been successful an examination of a sample of beans will show each to have a fissured interior, chocolate brown (Forastero) or cinnamon (Criollo) in colour. Unfermented and partly fermented beans, which are slaty and purple coloured, respectively, in the case of Forastero, should be absent.

Fermentation in holes in the ground fortunately finds little application – the hole can easily become water-logged and the sweatings cannot drain away. It is probably true that more beans are fermented in heaps (Inset 3) than in any other way. A conical mound of 500 to 1,000 lb of beans is formed on a layer of banana

*Higher maxima are sometimes obtained.

or plantain leaves, which are also used as a cover when the heap is complete. To achieve a more uniform product, it is desirable to ferment the beans in a wooden box – the so-called 'sweat box'. A series of holes in the floor of the box allow the sweatings to drain away and care has to be taken to see that the wood used in construction gives no taint to the beans, and that nails do not penetrate to the interior, for they can cause black marks to appear on the beans. It is often convenient to employ a set of three boxes arranged in a cascade. The beans are then shovelled from the upper to the middle box after two days, and from the middle to the lower after another two days have elapsed. These transfers have the effect of mixing the beans as well as aerating them. The capacity of the box varies considerably from one fermenting site to another; as long as the depth of beans within does not exceed about three feet a satisfactory fermentation is obtained. As with a heap, the beans are covered with a layer of leaves.

It has recently been claimed that small quantities of beans, i.e., 20–50 lb, can be fermented satisfactorily in thin layers on trays. This method would be a boon to the small peasant producer, but would be possible only if the recommended conditions are closely kept; if they are not there is a real danger that an undue proportion of the beans will be only partially fermented.

In all fermentation methods it is necessary to ensure two things: first, that the balance struck between heat production in the mass, and heat loss from it, be such that the temperature of the beans will rise to about 45°C and be maintained at this figure for two to three days; secondly, that the beans are aerated.

Drying

In some cacao-growing areas, such as those in Ghana for example, where the rainfall is not excessive, and the number of bright sunny days considerable, it is possible to dry fermented cacao beans in the sun in six to ten days. The beans are dried on the ground, or on trays (Inset 4), which must be covered when rain falls, or on drying wagons, i.e., large trays fitted with wheels

which run on rails, so that they can be run back under a shelter. These shelters can be kept to reasonable dimensions if the rails are so arranged that one wagon will run above another. An alternative protection is a movable roof, running on rails, so that it can be drawn over the beans lying on a fixed floor. Such methods have been in use in many places – West Indies, Central and South America, Indonesia, etc.

In other areas, less fortunate in their climatic conditions, it is necessary to use artificial heat to dry the beans, because to rely on the sun alone where the rain and cloud are excessive leads to the serious risk of mould. This is one of the worst defects in commercial cacao beans, since the unpleasant flavour it introduces persists throughout the process of manufacture.

Cacao dryers have been in general use for over 50 years and there is a record that they were discussed in Trinidad as early as 1865. The types have been numerous and various, and only the most important of those which can be found working at the present time will be described.

In the simpler types of artificial dryer, beans are dried by heating the drying floor below by hot air. Pipes are installed within the air space beneath the floor and through them circulate water from a boiler or the hot products of combustion from a wood fire or burning oil jet. The drying floor may permit the passage of hot air through the beans (Martin dryer), and the addition of a fan (Vis dryer) to draw off the moist air is an advance. The roof of the Martin dryer is sometimes constructed so that it can be run back in times of fine sunny weather and the drying process hastened by direct heat from the sun.

In the Cameroons dryer, the space between the flue pipes and dryer floor is filled with earth, and an uneven temperature distribution results, making more frequent raking of the beans necessary. Faulty construction is common, and smoke may come into contact with the beans thus causing off flavours. In the dryers of the stationary tray type (for example, the 'Chula') a blast of indirectly heated air is forced through a stack of metal trays, with wire mesh bottoms, and containing wet fermented beans. When the desired output of dry beans is very large, and

B

tray loading and unloading becomes laborious, it is an advantage to use a continuous dryer such as the Büttner. An endless row of trays passes spirally down a vertical cylinder through which hot air is circulated.

The Gordon and McKinnon dryers have achieved a large measure of popularity; a large cylinder rotates slowly about a horizontal axis, along which hot air flows and escapes into compartments containing the beans. The rotation of the cylinder leads to the rubbing of the beans against each other, and, when dry, they exhibit the polished appearance prized by some cocoa buyers. The shell is also rather thinner on account of the abrasive action of one bean on another, and there is an increased incidence of broken beans.

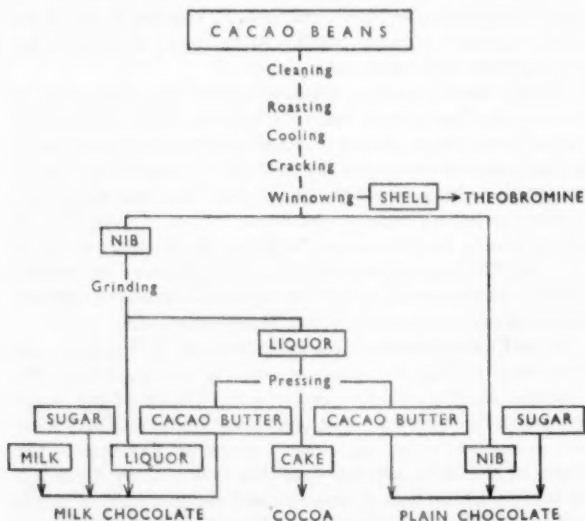For success it is essential with all dryers that no chance be

Fig. 1. Schematic flow sheet of cocoa and chocolate production.

given for the beans to be exposed to the products of combustion or taint will result.

Uses of the Cacao Bean

The cacao bean is mainly used for the manufacture of cocoa and chocolate, and a flow sheet showing the outlines of the processing involved is given opposite. Cleaning of the bean is followed by roasting, which develops flavour and aroma, and loosens the shells. After cooling, the beans are cracked and the shell winnowed away, leaving the cracked cotyledon known as nib. Cacao butter is extracted from the ground nib by pressing and the resulting cake is pulverized to give cocoa powder. The extracted butter is used in the preparation of chocolate by incorporating it in a mixture of nib and sugar, for plain chocolate, and in a mixture of liquor, sugar and milk, to produce milk chocolate. Chocolate which is used to cover confectionery is usually made thinner by the addition of a relatively greater amount of cacao butter.

Cacao butter itself finds a use in pharmacy, because it is hard and brittle at room temperature yet melts at blood heat. Theobromine occurs in the shell and nib, and has some medicinal purposes, but its greatest use is for the preparation of caffeine. Shell, which accounts for 10–12 per cent of the bean, may serve as a cattle food as well as a source of theobromine.

CHEMISTRY OF CACAO

The use of the term 'cacao fermentation', although well established, is not entirely satisfactory. Breakdown of the pulp is a true fermentation but reactions in the cotyledon are not. It has already been stated that the process of fermentation is one of the most important of the many involved in the production of cocoa and chocolate. The subsequent chocolate flavour will be poor if it is not properly conducted and will be virtually absent if the process is omitted. During fermentation, changes occur in the cotyledon of the bean and also in the surrounding pulp. Some chemical constituents are altered while others are destroyed, synthesized, or exuded in complicated processes as yet

incompletely understood. Carbon dioxide is produced by bacterial action in the pulp and from the respiration of the cacao bean, the latter contribution ceasing on the death of the bean.

Pulp

The main role of the pulp in fermentation is as a site of exothermic reactions which provide a suitable pH, and sufficient heat to raise the temperature of the cotyledon of the bean, for the all-important reactions concerned in the production of chocolate flavour to take place. A minor contribution might be to add to the subtle flavours found in beans in company with the main chocolate flavour.

An approximate analysis of the pulp is as follows:

Water	80·0
Citric acid	1·5
Glucose and fructose	15·3
Sucrose	0·6
Pectin	1·0
Amino acids: glutamic, aspartic	
Asparagine	

The sugars are broken down by the action of yeasts and bacteria, pectic enzymes disrupt the cells, and much of the pulp runs away as the sweatings. In the first day, yeasts convert the sugar in the pulp to ethyl alcohol which attains a concentration of 3–4 per cent. Acetic acid bacteria develop rapidly thereafter and in the next two or three days predominate over all other types. For this conversion of ethyl alcohol to acetic acid, oxygen is needed. The acetic acid so produced passes through the testa and into the cotyledon, and is probably mainly responsible for the fall in the pH of the latter from its initial value of about 6·6. Lactic acid bacteria only appear in the parts of the heap where aeration is poor. There are, of course, other organisms there that do not take part in the fermentation reactions.

Aeration is facilitated by mixing, and also by the collapsing of the pulp, thus enabling air to be drawn into the mass of warm beans from the sides of the heap, or the holes in the bottom of the sweat box. Aeration must not, however, become excessive,

or undue cooling will occur and other unwanted effects result as well. In the later stage of fermentation (3–6 days) the total number of bacteria becomes less, probably because the high temperature is unfavourable to them .

Initially, the pH of the pulp is about 3·7 (Table II) – due to citric acid, to which the testa is impermeable, and during fermentation it is lost in the sweatings. The citric acid – a relatively strong acid – is lost from the pulp at the same time as acetic acid is produced, and the net observed effect is a rise in pH. Should fermentation be unduly prolonged beyond six days, the pH of the residual pulp, and the high temperature, encourage the multiplication of other bacteria, whose metabolic products adversely effect the flavour of the subsequent chocolate. The dead beans are, in fact, decaying and putrefying, hence the need to move them to the drying trays or the drying machine at the right time.

Shell

Little work has been done on the shell, which accounts for about 10–12 per cent of the weight of the dry fermented bean, and it is of slight economic importance at the present time.

Cotyledon

At the beginning of fermentation the bean is, of course, viable and remains so for about 36 hours, until it is killed by the combined effects of high temperature and increased acidity, both resulting from reactions in the pulp already outlined. There is a conflict of opinion, however, due mainly to the absence of an objective assessment of chocolate flavour, as to whether this period in the fermentation heap, when the bean is viable, is necessary for the *full* development of chocolate flavour. Two types of experiments have been done to test this: (1) in the laboratory beans were raised rapidly to a temperature of 45° C which was then maintained for several days; (2) several hundred pods were kept at $-12°$ C for a week before breaking, extracting the beans, and allowing them to ferment in a box. Beans from both experiments did, in fact, have chocolate flavour. In

this second experiment, the temperature cycle followed fairly closely that of an untreated control fermentation, showing, incidentally, that the heat of 'incipient' germination made a negligible contribution to the total heat of fermentation.

The more important constituents of the cotyledon are – in decreasing order of abundance – cacao butter, carbohydrates, polyphenols, proteins, theobromine, and caffeine.

(a) Cacao Butter

Cacao butter is the major constituent of the cotyledon (55 per cent of the dry weight) but appears to undergo no change in fermentation: it is pale yellow in colour, non-greasy to touch, and hard and brittle at temperatures less than 27° C. The plastic range is short, and above 27°C it becomes soft, melting in the mouth and giving a pleasing sensation. It is the good fortune of consumer and manufacturer alike that cacao butter exhibits these unique physical properties! Cacao butter is polymorphic and the melting point varies from one modification to another – a property partly responsible for the need of technical skill in the moulding of chocolate preparations. A good sample of butter will contain less than 0·5 per cent of free fatty acid and have an iodine value of 38. The constituent glycerides are few in number and contain the acids oleic, stearic, and palmitic, in approximately equal proportions, together with a little linoleic: the predominating glyceride is the 2-oleo-palmito-stearin, and current research in this field is directed at discovering the structure of the minor glycerides.

It may be mentioned here that the percentage phosphatide content of the bean is fractional, with some indication that a small decrease takes place in fermentation.

(b) Carbohydrates

With regard to the carbohydrate content (15 per cent) of the cotyledon, the picture is far from complete. Evidence that the starch content (originally 6 per cent) stays unchanged in fermentation has been disputed. A number of sugars has been detected – a pentose, a methyl pentose, fructose, glucose, raffinose,

stachyose, and others, as yet unidentified. In total they account for about 1 per cent of the dry weight. The residual carbohydrate is made up of cellulose, pectin, etc.

(c) Polyphenols and proteins

The two classes of compounds most affected in fermentation are the proteins and the polyphenols (each accounting for about 8 per cent of the dry weight) and both have been the subject of considerable research.

The polyphenolic compounds are found in special storage cells in the cotyledon and when death occurs by the combined action of high temperature and lowered pH, they migrate to the site of the enzymes and undergo chemical action. The polyphenolic fraction is made up of: 2 anthocyanins (0·5 per cent), at least 3 leucoanthocyanins (2·5 per cent), 4 catechins (3 per cent), mainly (−)-epicatechin; and lastly, complex polyphenols (2 per cent). The 2 anthocyanins, 3-β-D-galactosidyl- and 3-α-L-arabinosidyl-cyanidin, account for the purple colour of the cotyledon of a fresh (unfermented) Forastero bean but are absent from Criollo. After the death of the bean a glycosidase enzyme hydrolyses them, liberating galactose and arabinose respectively, leaving cyanidin which is converted to a colourless pseudo base. Optimum, though not critical, conditions for this glycosidase activity are a temperature of 45° C and a pH of 4. Oxygen is not required for the reaction. Compounds included in the complex polyphenolic fraction inhibit this reaction while others in the fraction are themselves hydrolysed. During this period little change occurs in the catechins and the leucoanthocyanins though there is some loss by exudation. In the latter half of fermentation when the pulp has been broken down and air enters the mass of beans more readily, reactions begin which are only completed in the drying phase. Polyphenol oxidase plays a part here and the polyphenols undergo oxidative browning, hence the chocolate brown colour of the well fermented and dried bean of commerce.

For the polyphenols the fermentation and drying processes can be divided, chemically, into a hydrolysis, not requiring air,

of glycosides, followed by an oxidation, for which air is neces-
sary, of non-glycosidic polyphenols and polyphenolic aglycones.
There is also the tanning by the polyphenols of proteins, includ-
ing enzymes. If, because of unsatisfactory fermentation condi-
tions, polyphenol oxidase activity precedes glycosidase activity,
purple beans will be produced : it is known from *in vitro* experi-
ments that epicatechin oxidation products will inhibit glyco-
sidase activity. It will be noted that there is a slight conflict in
the oxygen requirements of the fermenting mass : sufficient must
be available for the bacteria to proliferate and raise the tem-
perature adequately, yet there must not be enough for oxidase
activity to occur before hydrolysis by the glycosidase.

With regard to the protein, an account of a detailed, though
not complete study has been published recently, which was
carried out in Trinidad on Trinitario beans. Protein is lost in two
ways : (1) by hydrolysis to peptides and amino acids, and (2) by
conversion to insoluble forms, involving tanning by poly-
phenolic compounds. As fermentation proceeds, free amino acid
increases, attaining a constant value after three days. The
soluble peptide content also increases, but reaches a maximum
after three days, after which it subsequently falls. In contrast,
the more complex soluble peptide increases in this latter stage
and protein decreases throughout. The net gain in total nitrogen
observed in the second day is due to diffusion into the cotyledon,
from the testa itself, and across it, from the pulp. At the begin-
ning of fermentation only seven amino acids are detectable, with
some also present as their amides, but the number increases to
eighteen. Since similar changes occur in a poor fermentation,
though to a lesser degree, there is the possibility that the protein
content could prove an objective measure of the quality of
fermentation. It is unfortunate that data are insufficient to en-
able any correlation to be seen between the progress of the
changes described and the time of death of the bean.

(d) Theobromine and caffeine

Theobromine, the principal alkaloid from cacao (also found
in cola nuts and tea) is confined exclusively to the cotyledon

(1·5 per cent) if the bean is examined at the time of its removal from the pod. In fermentation there is a diffusion, which starts at the death of the bean, from the cotyledon into the testa, and the dry bean contains equal percentages in both the cotyledon and shell. Caffeine is also present in cacao, but to about one-tenth of the extent of theobromine.

Flavour and aroma

'Chocolate flavour' has frequently been referred to, but from a chemical standpoint, little can be said either about it or about the aroma of cacao products other than that fermentation and drying (in the country of cultivation) and roasting (in the cocoa and chocolate factory) are the processes most concerned.

Chocolate flavour cannot be attributed to only one or two chemical compounds: it is obviously due to a balance between a large number, and it will become better understood as research on the chemistry of fermentation continues. Gas chromatographic techniques should be of great assistance in helping to solve problems connected with aroma. The day when chocolate flavour and aroma can be assessed chemically, and therefore objectively, is still far in the future.

ELECTROPLATING TODAY

D. J. FISHLOCK

FEW engineering practices have proved as controversial as electroplating. This widely applied method of decorating and protecting less chemically stable structural metals has, for various reasons, tended to fall into disrepute in some quarters. In this article it is hoped to examine some of the problems, and describe some of the progress and developments, that are taking place in this complex branch of applied science.

ORIGINS AND DEFINITIONS

At this point a brief review of the origins of electroplating is in order. The craft of electroplating, or electrodeposition, is the art of producing films of metal with closely specified physical characteristics from a solution of its salts. The term electrodeposition, although often used synonymously with electroplating, is reserved within the trade for relatively thick deposits such as those needed in electroforming, in the repair of worn or over-machined components, and in the protection of chemical plant. Electroplated coatings, on the other hand, are generally very thin – rarely above 0·002 inch, and often only 0·0002, in depth – and should be fine-grained, strongly adherent, smooth or bright in appearance, and of low porosity if they are to be of value. The distinction from electro-refining lies in the relative unimportance of the physical properties of the deposit laid down in this process, provided that the deposit is sound enough to withstand handling.

Electroplating was born at the start of the nineteenth century shortly after Nicholson and Carlisle, in 1800, first electrolysed water into its constituent gases. The first plating patent was issued in 1810, and by 1837 jewellers were practising gold and silver plating, using batteries to supply the current. Large-scale

commercial plating began about the middle of the century, but the full exploitation of its possibilities had to await the invention of the low voltage D.C. generator in 1874. Then followed a gradual improvement of solution formulae, the empirical discovery of brighteners and other small additions to the solution which could so efiectively influence the characteristics of the deposit, and an app eciation of the fundamental importance of correct and thorough pretreatment prior to plating.

Until well into the present century much of the industry lay in the hands of individual craftsmen who had acquired their knowledge of an intricate and often extremely vexatious art by the laborious process of trial and error. Such hard-won assets were jealously preserved and handed down from father to son – relatively little information being published. Ironically, it has taken two world wars to produce a real understanding of the importance of electroplating. The importance of metal finishes – not merely nominal ones, but finishes that would preserve components and articles perfectly under the most diverse and adverse conditions – were only gradually appreciated. Decorative finishes, again of lasting quality, came into considerable demand after the first world war. The processes available to fulfil these demands were the result of extensive research by plating supply houses and independent research organizations. These institutions had, however, to overcome the reluctance of a strongly conservative industry to make changes, and nowhere was this in greater evidence than with regard to the plating solution itself.

The plating solution

The nineteenth and early twentieth century plater had relatively few metals at his disposal. In addition to silver and gold the only ones of significance were nickel, copper, zinc, brass, and to some extent tin and iron. Plating solutions, the essential ingredients of which are metal ions and usually an electrolyte to improve the conductivity, were based on soluble and inexpensive salts such as chlorides and sulphates. Only one complex ion type of solution was available, that based on cyanide. Thus

cyanide formulations were universally used for silver, gold, and brass, and for some copper and zinc baths; sulphate for nickel and iron, and often for copper and zinc; while chlorides also featured prominently in later nickel solutions and for tin and iron. Nitrate, the third simple radical, finds little application, because it is unstable and liable to be reduced to ammonia at the cathode. The past two decades have seen the introduction of many more metals, including chromium, rhodium, cadmium, cobalt, indium, and aluminium, and a host of useful alloys which include tin/zinc, tin/nickel, tin/copper, speculum, nickel/cobalt, and various combinations of silver and tungsten.

The plating solution is probably the most mutable item in any production line, and it says a lot for the skill of an experienced plater that he should operate so consistently under the most unfavourable conditions. Since much of the knowledge of the idiosyncrasies of a given bath would have been imparted to him, probably by his father, he would yet be left to complete large gaps in this knowledge in the only available way – by experience. His reluctance to tackle entirely new solutions presented by scientists with scant appreciation of production problems is, therefore, readily understood. True, the scientist offered some tempting inducements: faster plating solutions that required minutes instead of hours, and gave deposits that needed less and eventually no polishing, or which, having plated out the metal, would then polish it when the current was reversed; solutions that would deposit metals and alloys hitherto unconsidered, with new and desirable properties, to mention but a few features.

Against these, however, had to be weighed some material drawbacks. No longer, in many cases, could the plater maintain his solution with a hydrometer and practical know-how. He needed an analyst, and preferably one on the spot. No longer, he found, were his solutions so insensitive to impurities. Items as varied as bananas, coins, emery powder, and even a dead dog have been dredged up from plating vats! Often he found it hard to assimilate radical changes in plating practice. One of the reasons for the slow acceptance of chromium plating, notwithstanding its superlative attributes, was the very much higher currents

than were customary, needed to persuade the metal to plate out at all, let alone at a reasonable rate. A similar situation exists with the new nickel and silver plating solutions, which also need much heavier currents to gain full advantage.

Even today there are some very well-founded objections to large and sudden changes in plating practice. An economic one lies in the capital cost of a large and usually rather inflexible automatic plant. A machine such as that illustrated in Inset 9 would probably have to be scrapped if, for instance, a nickel solution plating three times as fast were incorporated. Again, alloy plates offer many advantages over pure metals, often blending the best features of their constituents; many solutions co-depositing two and even three metals have been evolved which work perfectly – under laboratory conditions. In the workshop eight out of ten of them prove an unqualified nuisance. Analytical practice, too, often lags behind solution formulations, with the result that the plater is presented with some unanalysable concoction that can only be maintained (and even then there is often some doubt) by the supply house sponsoring it. In addition, more elaborate electrical and chemical plant and control equipment are often essential concomitants of this progress (Inset 10).

PLATING MECHANISM

The physico-chemical mechanism that promotes the transition of metal ions into solid atoms in a crystal lattice remains largely unexplained. The difficulties involved in probing into this phenomenon, which undoubtedly holds the clue to stronger, more ductile, more corrosion-resistant deposits, are indeed formidable. The ion-to-atom transition takes place within a thin film of electrolyte known as the cathode film, which is probably less than 0·01 inch deep, and is in contact with the cathode while electrolysis is in progress. The existence of the cathode film has been confirmed by several ingenious techniques, the most rewarding of which is Brenner's freezing cathode.[1] Using a hollow cylindrical cathode into which he introduced a freezing mixture, Brenner was able to solidify the contiguous electrolyte

and could then machine off successive layers of known thickness for chemical analysis. In this way he was able to show that the composition of the cathode film bore scant physical or chemical relationship to that of the main electrolyte. In nearly neutral nickel solution, for instance, the pH of the cathode film was sufficiently high for nickel hydroxide to be in suspension, and to become occluded in the deposit; again, a marked concentration gradient of nickel ions exists in this region.

The actual deposition of metal depends on the existence of a sufficiently high potential difference between the metal ions in the cathode film and the negatively charged cathode. When neutralized the ions appear to take their places in a crystal lattice unit, which for many electrodeposited metals is a face-centred cube of 14 atoms. There are two current hypotheses: one is that the metal atom discharges at the point where it is required to further the crystal structure, or, if no such point exists within its sphere of influence, discharges at a slightly higher potential to initiate a new lattice unit. The other suggests that atoms are discharged at random over the cathode surface and initially are endowed with a certain mobility which enables them to locate their most appropriate site in the lattice unit.

A greater understanding of the true mechanism would certainly pave the way to much more versatile electrodeposits and less troublesome solutions. It could well explain the mechanism of brightening by traces of organic compounds, and help us to eliminate the loss in ductility which appears inherent in the harder bright deposits such as those of nickel; it could explain such characteristics as internal stress and porosity which reduce the mechanical strength and corrosion resistance of many deposits; and it could aid the electrochemist to deposit a metal with physical characteristics closely defined for a given purpose. Work is proceeding, particularly in British universities, to acquire a deeper understanding of these problems. In this work three techniques appear to hold outstanding promise of persuading the electrolyte to yield up its secrets. One is the use of electron-diffraction apparatus for examining the coating structure – and especially the structure of the first layers of atoms to

be deposited. Recent experiments have indicated that a temperature of several hundred degrees centigrade exists within the surface layers of electrodepositing atoms and that there is a close similarity between electrodepositing and condensing films of metal.[2] The second, used in conjunction with X-ray diffraction, interferometrical and optical goniometrical experiments, is the use of a 16-mm. ciné-camera in conjunction with a microscope to take a film of the cathode during electrolysis.[3] The third is the use of radioactive tracers to track the movements of atoms.

NEW PLATING SOLUTIONS

The limitations of simple inorganic solutions based on sulphates and chlorides are numerous. These are corrosive ions, usually used in the presence of excess free acid to increase conductivity, and this poses many problems in handling and containing them. They also tend to give relatively coarse-grained deposits, particularly if addition agents are not used, this property being relatable to their high degree of dissociation. Often, too, this results in displacement reactions with metals to give badly adherent plating. Further, in most cases there are definite upper limits to the rate at which metals can be deposited from them.

Cyanide solutions, although containing complex ions, and free from some of the above limitations, nevertheless have one big drawback in their toxicity. Thus there is ample justification for development work on entirely new solutions.

Sulphamates

These are the most recent salts to find commercial application, little being known of them prior to about 1950. They are the salts of amido-sulphonic acid, $H.SO_3.NH_2$, and they exhibit many useful attributes in plating solutions. They are stable, and give highly conductive solutions which can be worked faster than those of simple salt, while the deposits themselves are smooth and fine grained, and if hard, as is nickel, have little internal stress. Sulphamates have been successfully used for the deposition of cobalt, iron, cadmium, zinc, lead, silver, rhodium, and indium, and, most important of all, nickel.

Unfortunately, although very extensively investigated and promoted, particularly by Piontelli in Italy, the very high cost of the acid and its salts militates against extensive application. This factor, however, could well prove a minor one even now in the case of precious metal solutions, while the price may be expected to fall with increasing demand.
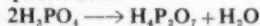
Fluoborates

Probably the most useful of the new ions is fluoborate. This is not strictly a complex salt, since it is highly ionized in solution; yet in many ways it reacts as if it were. The acid is highly stable, and is produced by the interaction of boric and hydrofluoric acids:

$$H_3BO_3 + 4\,HF \longrightarrow HBF_4 + 3H_2O$$

In the solutions used for plating some 1 to 5 per cent excess boric acid is present to ensure stability (the solution will not then attack glass, for instance), and also to give more conductive electrolytes with less tendency to yield nodular deposits. They have found extensive application in the plating of tin, copper, zinc, nickel, and indium, and most significantly, lead. Today the lead fluoborate solution is the most important of some four or five electrolytes for this metal. Its characteristics are similar to those of sulphamate solutions, but the solubility and conductivity are higher, while any difficulty hitherto experienced in preparing fluoborates *in situ* is now obviated by the sale of metal concentrates. Other important applications lie in high speed continuous strip plating with tin and zinc, and in the deposition of tin alloys such as the solderable tin/lead and tin/cadmium alloys.

Pyrophosphates

These are derived from pyrophosphoric acid, obtained by heating orthophosphoric acid:
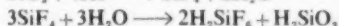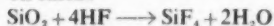
$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$

The ortho salts similarly yield pyrophosphates. These have found an important role in the replacement of cyanide copper and zinc solutions. Pyrophosphates of these metals are insoluble,

but dissolve in excess potassium pyrophosphate to give a non-toxic and highly conducting solution, with a pH of 8 to 9. For copper the pyrophosphate bath replaces both the corrosive acid sulphate electrolyte, and the hot cyanide which will not produce smooth deposits of depth greater than about 0·001 inch. Unfortunately a cyanide solution is still required for a preliminary 'flash' deposit on ferrous metals to avoid the formation of a displacement deposit. Pyrophosphate salts are now cheap enough to be attractive, while the simple operation of the bath and the smooth, fine-grained plates obtained justify their consideration. They appear to have found little commercial application as yet, other than for plating zinc and copper, and very recently for tin-bronze and nickel.

Fluosilicates

These derive from fluosilicic acid, H_2SiF_6, formed by the action of HF on silica:

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$
$$3SiF_4 + 3H_2O \longrightarrow 2H_2SiF_6 + H_2SiO_3$$

These have not enjoyed the popularity that fluoborates command, although a few solutions, notably for lead, have been evolved. Since they are less costly than fluoborates, they are used in lead refining, while a secondary application is as a substitute for the sulphate catalyst in chromic acid electrolytes.

Chromium Solutions

Although the potential value of chromium as a decorative metal was appreciated many years ago, it was not until 1924 that a commercially practicable method of plating chromium was worked out. This method, basically unconventional in that it employs a strongly acidic solution of 6-valent chromic acid, and requires the presence of a critical amount of a small dimensional ion such as SO_4^{-2} to catalyse the deposition, is fundamentally unchanged today. In operation this solution offers many advantages, but its extremely low electro-chemical efficiency (10 to 15 per cent) combined with the high valency makes the rate of deposition low indeed. Again, the catalyst content is

Unfortunately, although very extensively investigated and promoted, particularly by Piontelli in Italy, the very high cost of the acid and its salts militates against extensive application. This factor, however, could well prove a minor one even now in the case of precious metal solutions, while the price may be expected to fall with increasing demand.
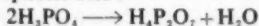
Fluoborates

Probably the most useful of the new ions is fluoborate. This is not strictly a complex salt, since it is highly ionized in solution; yet in many ways it reacts as if it were. The acid is highly stable, and is produced by the interaction of boric and hydrofluoric acids:

$$H_3BO_3 + 4HF \longrightarrow HBF_4 + 3H_2O$$

In the solutions used for plating some 1 to 5 per cent excess boric acid is present to ensure stability (the solution will not then attack glass, for instance), and also to give more conductive electrolytes with less tendency to yield nodular deposits. They have found extensive application in the plating of tin, copper, zinc, nickel, and indium, and most significantly, lead. Today the lead fluoborate solution is the most important of some four or five electrolytes for this metal. Its characteristics are similar to those of sulphamate solutions, but the solubility and conductivity are higher, while any difficulty hitherto experienced in preparing fluoborates *in situ* is now obviated by the sale of metal concentrates. Other important applications lie in high speed continuous strip plating with tin and zinc, and in the deposition of tin alloys such as the solderable tin/lead and tin/cadmium alloys.

Pyrophosphates

These are derived from pyrophosphoric acid, obtained by heating orthophosphoric acid:
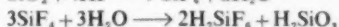
$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$

The ortho salts similarly yield pyrophosphates. These have found an important role in the replacement of cyanide copper and zinc solutions. Pyrophosphates of these metals are insoluble,

but dissolve in excess potassium pyrophosphate to give a non-toxic and highly conducting solution, with a pH of 8 to 9. For copper the pyrophosphate bath replaces both the corrosive acid sulphate electrolyte, and the hot cyanide which will not produce smooth deposits of depth greater than about 0·001 inch. Unfortunately a cyanide solution is still required for a preliminary 'flash' deposit on ferrous metals to avoid the formation of a displacement deposit. Pyrophosphate salts are now cheap enough to be attractive, while the simple operation of the bath and the smooth, fine-grained plates obtained justify their consideration. They appear to have found little commercial application as yet, other than for plating zinc and copper, and very recently for tin-bronze and nickel.

Fluosilicates

These derive from fluosilicic acid, H_2SiF_6, formed by the action of HF on silica:

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$
$$3SiF_4 + 3H_2O \longrightarrow 2H_2SiF_6 + H_2SiO_3$$

These have not enjoyed the popularity that fluoborates command, although a few solutions, notably for lead, have been evolved. Since they are less costly than fluoborates, they are used in lead refining, while a secondary application is as a substitute for the sulphate catalyst in chromic acid electrolytes.

Chromium Solutions

Although the potential value of chromium as a decorative metal was appreciated many years ago, it was not until 1924 that a commercially practicable method of plating chromium was worked out. This method, basically unconventional in that it employs a strongly acidic solution of 6-valent chromic acid, and requires the presence of a critical amount of a small dimensional ion such as SO_4^{-2} to catalyse the deposition, is fundamentally unchanged today. In operation this solution offers many advantages, but its extremely low electro-chemical efficiency (10 to 15 per cent) combined with the high valency makes the rate of deposition low indeed. Again, the catalyst content is

critical and none too easy to assess accurately and quickly. The solution, however, has proved intractable towards significant modification.

One improvement has been to incorporate a slightly soluble catalyst, so that the bath remains saturated with respect to the catalytic ion. Since it is the ratio of catalyst to chromic acid, rather than the absolute concentration of constituents, that is critical, this method of regulating the catalyst content can be used. In practice, excess strontium sulphate is added, and the balance, since it is not quite soluble enough, made up with sulphuric acid; any rise in the sulphate to chromic acid ratio then causes strontium sulphate to precipitate and adjust the ratio. There is also news from Russia of developments with a cold chromic acid solution containing ammonium fluoride.

Organo-metallic Solutions

These represent a complete departure from conventional plating practice, in that alcoholic solutions of organo-metallic salts are used and that they are of unusually high metal concentration in many cases. They are not intended for vat plating, however, but for the localized deposition of metal. The solution is retained in a thick porous pad which surrounds a high-purity carbon anode, electrical connexion being made to the anode and work-piece. The work is then rubbed or stroked with the saturated pad. (See Inset 11.)
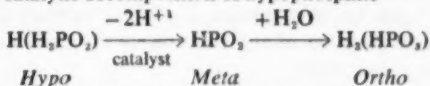
The practice of brush plating is not new, but hitherto only conventional metal salts solutions have been used. Under these conditions the conductivity of the pad was extremely poor, while such deposition as did take place caused marked changes in the limited amount of solution retained in it, and undesirable quantities of acid rapidly accumulated as a result of metal deposition. Not only are the new solutions highly conductive but, since the anions are organic, they decompose electrolytically to form only hydrogen, carbon dioxide, and steam, all of which are gaseous. Over small areas plating is extremely rapid because the conductivity and high working temperature (boiling point) of the solutions allow currents that would be regarded as incon-

ceivable in vat plating to be used with impunity. These factors and the rubbing action probably account for some of the unique features of the plates formed.
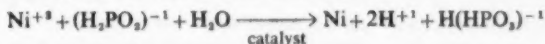
The solutions are usually based on an organic salt, such as an amino metallic one, together with an alcohol and a wetting agent. The chromium solution, for instance, can comprise an amino-oxalate of chromium such as Gregory's salt $[(NH_4)_2, Cr(C_2O_4)_2]$, methyl alcohol, and an alkyl amine wetting agent. The chromium content is about 80 grams per litre, which is actually lower than in conventional solutions, since the latter are unusually high in metal. In the case of other solutions, however, the metal content is much higher than normal, e.g., rhodium 20 g/l. compared with 1 to 2 g/l., and silver 280 g/l. compared with 18 to 33 g/l.[4]

CHEMICAL PLATING

Not strictly electroplating solutions, but closely related, are some recently developed formulations for chemically depositing sound, adherent deposits of certain metals, chiefly nickel. The essential constituents are a supply of metal ions and sodium hypophosphite, the metallic salt being continuously reduced in hot acid solution in the presence of a catalyst. Few metals, one of which, however, is nickel, are catalytic in this reaction, but immersion deposition with the liberation of hydrogen takes place at the surface of iron, aluminium, copper, and carbon, thus depositing enough atoms of nickel to initiate catalytic plating.[5] The reactions involved can be summarized in three equations: first the catalytic decomposition of hypophosphite

$$H(H_2PO_2) \xrightarrow[\text{catalyst}]{-2H^{+1}} HPO_2 \xrightarrow{+H_2O} H_2(HPO_3)$$

$$\textit{Hypo} \qquad\qquad \textit{Meta} \qquad\qquad \textit{Ortho}$$

secondly, the catalytic reduction of nickel ions

$$Ni^{+2} + (H_2PO_2)^{-1} + H_2O \xrightarrow{\text{catalyst}} Ni + 2H^{+1} + H(HPO_3)^{-1}$$

and thirdly, the formation of nickel phosphide, which appears in the deposited metal

$$(H_2PO_2)^{-1} + 3Ni^{+2} + 7H^{+1} \xrightarrow[\text{catalyst}]{} Ni_3P + 5H^{+1} + 2H_2O$$
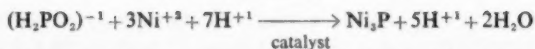
The last reaction arises as a result of an absorbed layer of nascent hydrogen on the metal surface, and accounts for the phosphorus in the deposit.

The phosphorus content, about 9 per cent in the case of the most highly developed of the commercial processes – Kanigen plate – no doubt accounts for some of the attractive features of the deposit, including its high corrosion resistance, low porosity, and good mechanical properties.

The original solutions tried were costly, ephemeral, and by electroplating standards slow to deposit, but the incorporation of a rather impressive number of additional reagents has radically changed the position in some respects. First, the pH of a working bath changes rapidly, and results in a heterogeneous, laminated plate. Buffering salts and continuous alkali feeds hold the value within the fairly narrow optimum range. The nickel orthophosphite which accumulates by decomposition of the reducing agent is slightly soluble, but if allowed to precipitate would rapidly initiate the complete catalytic decomposition of the solution. This salt is therefore chelated to maintain it in solution and thus stabilize the bath. Unfortunately the chelating agents affect the rate of deposition adversely, and accelerators must be added to counter this; soluble fluorides and short chain aliphatic dicarboxylic acids are examples, both of which decrease the stability of the hypophosphite molecule. Then, because some precipitation is unavoidable, inhibitors are added which render precipitates less liable to initiate catalytic decomposition. Thus the final solution is a highly complex chemical mixture the function of the constituents of which are often interrelated. See Table I.

To the analyst this mixture is a nightmare; in practice it is maintained by an elaborate regeneration system based on pH measurement, in which all constituents are replenished on a proportionality basis. The solution still has a finite life due to phosphite accumulation, but extensive industrial development has extended this to eminently practical lengths. Again, this is

TABLE I

Constituents of Chemical Nickel Solution		
Substance	*Primary Function*	*Incidental Influence*
Nickel ions	source of metal	–
Hypophosphite ions	reducing agent	source of P in deposit
Chelating compounds	complexing orthophosphite	slow down plating rate
Stabilizers	as above	slow down plating rate
Accelerators	increase instability of $H(H_2PO_2)$	brighten deposit and buffer pH
Buffering salts	stabilize pH	–
Inhibitors	decatalyse pre-cipitates	–

an instance of a formulation which, despite its complexity, is perfectly amenable to control.

Future developments in chemical plating hold promise of techniques for depositing copper and precious metals, and possibly chromium alloys. The capital cost of the regeneration equipment is considerable, but some of the processes at present in the development stage require much less elaborate maintenance systems. Even today, and certainly in the near future, chemical plating should supplant many engineering applications of electroplating, such as the repair of worn or over-machined parts, and the protection of very intricate articles which cannot be electroplated to an adequate thickness on all significant surfaces.

SOLUTIONS FOR ALUMINIUM

Strongly electronegative metals such as aluminium, beryllium, titanium, and magnesium offer an attractive challenge to plating chemists, both from an academic and, particularly in the case of aluminium and titanium, from a practical viewpoint. There are

at least two interesting outlets for electrodepositing aluminium coatings; one is as a protective (and, with further processing, highly decorative) finish for ferrous metals, and the other is in electroforming electronic components. The difficulty lies in the disparity in deposition potential between these metals and hydrogen, and the consequent ease with which hydrogen is released in preference from aqueous electrolytes. Fused salt and organic electrolytes therefore offer the only alternatives.

Much interesting work has been done with various organic solutions, at least four of which can be induced to plate out aluminium.[*] The most promising appears to be one comprising

Aluminium chloride	300 g.
Lithium hydride	6 g.
Diethyl ether	1 l.

Unfortunately, not only is this solution costly, highly inflammable, and relatively unstable, but it is decomposed by traces of moisture. Thus, although it yields plates of some promise, since it must be used in a special air-tight vat and for obvious reasons under the closest supervision, its translation from laboratory to workshop appears highly improbable.

Another solution is based on Grignard reagents, and is made by dissolving aluminium chloride or iodide and an alkyl or halogen halide in benzene. This gives a solution containing diethyl aluminium bromide and ethyl aluminium dibromide.

$$3C_2H_5Br + 2Al \longrightarrow Al(C_2H_5)_2Br + Al(C_2H_5)Br_2$$
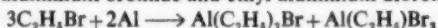
Aluminium triethyl and tribromide are probably also present. Sealed from the atmosphere, vats containing solutions of the carefully dried reagents would last for months; open, however, the electrolyte absorbs moisture and becomes inoperable in a few days.

A third method is based on a eutectic mixture of ethyl pyridinium bromide and aluminium chloride. It is used as a 32 per cent dispersion in toluene, kept in suspension by bubbling pure nitrogen through the electrolyte. The properties of the deposits obtained in this solution appear less promising than with the other methods.

One of the latest solutions, patented in 1956, is based on the

liquid complex NaF.2Al(C₂H₅)₃ obtained by direct combination of aluminium, ethylene, and hydrogen and subsequent reaction with anhydrous sodium fluoride in the absence of air.

This substance melts at 35° C to give a conducting liquid which can be used as an electrolyte at temperatures between 80° and 150° C, and at high efficiencies. The most attractive features of this solution are the low cost of preparation and the high purity of the deposits, but it appears little nearer a practicable workshop solution to the problem.

As regards the other electronegative metals, much less work has been done. Magnesium can be deposited from ethereal solutions of Grignard compounds, and beryllium from solutions of its salts in liquid ammonia. Titanium appears a little more promising, a potassium titanium fluoride/sodium chloride melt, used at 800° to 900° C in an atmosphere of argon, being one possibility, while a really hopeful discovery makes use of an aqueous sulphate solution—a reversion, paradoxically, to simple salts.

ADDITION AGENTS

Plating solutions are no longer essentially simple solutions, comprising a metal salt, and perhaps one or two other salts to facilitate operation or control, or modify the characteristics of the deposit. Today, they frequently include a diversity of substances, often organic chemicals, which are present in small amounts and known collectively as addition agents. The chemical plating bath already described is an extreme example, but frequently encountered plating additions are surface active agents, brighteners, and levellers. Brighteners, known since 1847 when the efficacy of traces of carbon disulphide in silver solutions for improving the lustre of the plate was first noted, include a host of organic and a few inorganic substances. In their absence deposits tend to become increasingly matt and rough as they build up. Many attempts, none universally successful, have been made to relate their structure to their effectiveness, but until very recently they continued to be discovered largely on an empirical basis. In the correct, and often closely defined

quantity, and when coupled with specified operating conditions, such as bath temperature and current density, they can often, especially in the case of nickel baths, exert an influence on the appearance and structure of the plate out of all proportion to their quantity. See Inset 12.

Levelling agents are a very recent discovery, which induce the deposit to plate preferentially into small recesses such as pits and scratches on the surface of the work. Thus the overall effect is to produce a plate which is smoother than the original surface (Inset 13). In combination with suitable brighteners this can mean that a finely ground article emerges highly polished from the vat. Both levellers and brighteners are lost by decomposition, adsorption, and co-deposition with the plate, but their complex constitution usually precludes close analytical control. Recourse must be made to rapid though not entirely satisfactory physical methods of control.

Another new addition is that of chelating agents. Very small amounts of many foreign substance accumulate in the solutions, through air-borne dusts, impure water supplies, or attack on the articles being plated. These impurities often adversely affect the quality of, in particular, decorative plates, and require expensive chemical treatments to effect their elimination. By adding very small amounts of chelating agents many such impurities can be complexed and their nuisance value thus minimized. These substances, examples of which include ethylenediamine tetra-acetic acid and its salts, are expensive, but their efficiency and the very small quantities needed tend to outweigh this drawback.

PHYSICAL INFLUENCES

The influence of several physical factors on the plating mechanism is a profound one; these include pH, temperature, solution agitation, and the D.C. current supply. Of them the last two are of especial interest in view of the marked effects they can on occasion exert on the deposit.

Agitation is important in many plating solutions because among other things it helps to ensure the rapid replenishment

of the cathode film and to displace gas bubbles adhering to the cathode. Normally it is supplied mechanically or by bubbling air through the electrolyte. If, however, the far more intense agitation produced by ultrasonic vibrations is used the effect is remarkable. Considerably higher currents can be passed through the solution without 'burnt', i.e., dark, poorly cohesive, deposits tending to form, while, depending on the metal being plated, quite marked changes in the physical characteristics of the deposit are obtainable. Nickel deposits, for instance, have been found to have a higher tensile strength and hardness, and a smaller grain size, while inadequate pre-cleaning of the base metal is less deleterious since the agitation displaces any traces of grease.

This form of agitation is induced by immersing in the vat a transducer, which vibrates piezo-electrically or magneto-strictively in sympathy with a high frequency alternating voltage. At very high frequencies this agitation is due purely to the vibration of the surface of the transducer, but at frequencies around and just above the audible limit, 18 kc/sec., a secondary turbulence caused by cavitation appears. This is due to vacuum pockets forming at the metal surface, to collapse later with explosive violence (Inset 14). The industrial possibilities of this discovery are closely related to the development of cheaper and more efficient ultrasonic generators. The valve generators used to produce the very high frequencies are expensive at industrially practicable outputs, but the discovery that the lower frequencies can be equally and even additionally useful can be utilized through the medium of rotary alternators.

It is only fairly recently that attention has been paid to the wave-form of the applied D.C. plating current, but under certain circumstances this can appreciably influence the deposit. The first indications were when it was found that the chromium plate deposited with a battery or with a 3-phase (fairly low ripple) D.C. current was appreciably brighter than when deposited with single-phase D.C. No explanation has been forthcoming, and no differences in the crystal structure of the deposits can be detected, but the fact remains incontestable. In

1947 a scientist at the Westinghouse Electric Co. invented
periodic reverse current plating, in which an irregular form of
alternating current is used instead of the customary D.C.
Although rather costly to generate, this helps to produce sub-
stantially smoother, more uniform, and more corrosion-resis-
tant deposits.

CONCLUSION

The obvious query arising from this account of electroplating
progress is whether scientific research has contributed materi-
ally to the quality of plating. Certainly the answer would often
appear to be an emphatic 'no' when at any rate the plating on
motor car exteriors is considered. Even in this field, which is a
pretty severe test for a finish rarely more than 0·001 inch thick,
it is a fact that the finish on the higher quality models are not
often at fault. On cheaper cars there is a tendency in Britain, at
least, to economize on the finish, a tendency often conspicuously
absent from their Continental and American counterparts.

Many utilitarian finishes have undoubtedly greatly improved
in quality, and contribute enormously towards reducing the vast
annual expenditure due to corrosion, while the development of
methods of plating light metals and alloys have an extremely
practical objective. Even the controversial chromium plate
shows promising signs of improving appreciably in durability
in the next few years – always providing, of course, that it is not
supplanted by some new finish. Recent work in bright nickel
plating has thrown much light on the most efficacious way of
operating some of the latest and rather difficult plating solu-
tions, while American developments using several layers of
nickel, each plated from a different solution, hold promise of
appreciably more corrosion-resistant undercoats for the still
very popular chromium plating. Further, the end of restricted
nickel supplies leaves no excuse for economies in thickness.

The above shows that research and development has borne
some impressive fruit in this field. Much remains to be investi-
gated, however. In most of the examples cited the surface of the
problem has only been scratched, and more intensive work can

confidently be expected to yield good dividends. In particular, work is needed in the sphere of transplanting new processes from laboratory into workshop, although in some cases, particularly in the development of highly electronegative metal plating processes, the existing techniques themselves call for radical modification before this can be visualized. A virile and fascinating field thus exists for scientists prepared to work in conjunction with both laboratory and production engineering staffs in what is at once one of the most perplexing yet often aesthetically most rewarding industries.

REFERENCES

1 Brenner, A.: *Proc. Amer. Electroplaters Soc.*, 1940.
2 Wilman, H.: *Trans. Inst. Metal Finishing*, 1955 32.
3 Pick, H. J., and Wilcock, J.: *Trans. Inst. Metal Finishing*, 1958.
4 Hughes, H. D.: *Trans. Inst. Metal Finishing*, 1956 33.
5 Gutzeit, G.: *Trans. Inst. Metal Finishing*, 1956 33.
6 Heritage, R. J: *Trans. Inst. Metal Finishing*, 1955 32.

TRACE ELEMENTS IN PLANT AND ANIMAL NUTRITION

A. B. CALDER

FOR many years it has been recognized that a certain limited number of chemical elements are essential for plant and animal nutrition. In the last thirty years in particular, considerable attention has been directed by agronomists to investigations dealing with the mineral requirements of plants and animals, the disease conditions associated with deficiencies, and in some cases excesses, of certain elements, and the remedial measures required for the control of these diseases.

Apart from the elements carbon, hydrogen, oxygen, and nitrogen, which together with phosphorus and sulphur form the organic constituents of living plant and animal tissues, it has been shown that the mineral elements calcium, potassium, magnesium, and iron are likewise essential for normal nutrition, while in addition the animal requires sodium and chlorine. This has been shown by the invariable presence of these elements in the living organism, and by culture experiments which have demonstrated that without them normal development cannot take place. It has further been shown that certain other mineral elements were present in plant and animal tissues although in very minute quantities of the order of several parts per million. Initially, however, their occurrence was regarded as accidental. Animals depend for their food on plants which in turn derive their nourishment from the soil. This food is taken up by the plant roots in the form of a solution, and it was considered reasonable to suppose that in addition to absorbing the essential mineral elements calcium, potassium, magnesium, iron, sodium, and chlorine, the plant simultaneously absorbed smaller amounts of these other minerals which happened to be in the soil. They

were, however, present in extremely small amounts, had no apparent role in the metabolic processes, and were consequently ignored. But comparatively recently, considerable advances in analytical techniques, together with more intensive studies of the factors responsible for normal growth, have established certain disorders of plants and animals as diseases due to deficiencies, and in some cases excesses, of one or more of these particular elements. These occur in minute amounts or traces and are accordingly termed *trace elements*.

These trace-element deficiencies or excesses may affect the health of the plant, or the animal consuming the plant, or both. For example, boron is an element shortage of which in the soil creates disease conditions in the plant, without producing an effect on the stock grazing thereon. On the other hand, cobalt would appear not to be essential for plant growth and development, but if present in inadequate amounts (<0·10 p.p.m.) in pastures, is associated with 'pining' in ruminants. In comparison, there are one or two elements, e.g., molybdenum, selenium, and lead, which can cause disease in the animal if present in the soil or growth medium in excessive amounts. Many of these trace-element deficiency diseases are so widespread as to be of the utmost economic importance, and as such, to warrant further investigations in relation to the elements concerned.

Problems of Trace Element Study

In the general study of trace elements, two main types of problem are involved: (a) the demonstration of the essentiality of particular elements and the role played by them in the plant and animal, and (b) methods of diagnosis and control of those diseases of plants and livestock associated with deficiencies of these elements.

With regard to the first problem, the essential nature of the trace elements was for many years overlooked on account of the difficulty of constructing diets for plants and animals entirely free from the elements. In plant development these were introduced into the culture experiments partly from the seed from which the plant developed, partly from impurities in the

water and nutrient salts used in preparing the culture solutions, and by solution from containing vessels. There also existed the possibility of atmospheric contamination. The same problem was presented in the study of animal nutrition, the main difficulty in obtaining proof of the essential nature of an element depending on the availability of synthetic animal foods free from the elements concerned.

In order to investigate the essentiality of a particular trace element, means had to be devised of preventing the introduction of foreign material from all the possible contaminating sources. For example, so-called pure analytical reagents often contain amounts of trace contaminants (e.g., Fe impurity in Na_2CO_3) and these may be sufficient in themselves to supply the needs of the plant and animal. It is therefore imperative to stress the need for the purification of all material used in this type of work, as for example the purification of Na_2CO_3 used in plant ash fusions and the avoidance of metal parts in water distillation apparatus. In this connexion, while various plant and animal diseases have been attributed to particular deficiencies, the possibility of interaction between two or more elements must not be excluded. The purification of chemicals free from trace contaminants has been discussed by Stiles (1951) where references to the preparation of pure culture media are to be found, and a full account of the use of sand and water culture methods in the study of plant nutrition is given by Hewitt (1952).

Regarding the role of the trace elements in plant and animal metabolism, recent research would appear to indicate that their function is catalytic in nature and concerned with the regulation of normal growth processes.

Analytical Techniques

In investigating the part played by trace elements in plant and animal nutrition it is essential that methods for their quantitative determination be available. The concentration of these elements in plant and animal material is so low that the ordinary methods of chemical analysis are not sufficiently accurate. During the last twenty-five years a number of physical methods of

analysis have been developed for the measurement of minute quantities of material, and it is possible by means of these to estimate with reasonable accuracy most of the trace elements in plant and animal matter. Absorptiometric and spectrographic analytical methods have mainly been used. The absorptiometer is a form of colorimeter incorporating photoelectric cells by means of which the depth of colour of a solution is matched against that of a standard solution, and thereby measured. In the spectrograph a small sample of the material to be analysed is placed in an electric arc, flame, or other suitable source of excitation, in such a way that the molecules of the sample are dissociated into their constituent atoms, which are then stimulated to emit radiation. This radiation is limited to certain wavelengths characteristic of the elements in the substance and of the conditions of excitation employed. The radiation is passed through a prism and recorded as spectrum lines on a photographic plate. Each line possesses a density or intensity of blackening, which, under suitable conditions, is a function of the concentration of the element excited. The spectrograph affords the most sensitive method of measuring small quantities of a large number of elements simultaneously, and provides a permanent record, so that results are available for future reference. In the analysis of trace elements in plants, soils and related material, attention must be drawn to the need for freedom from contamination at all stages of the procedure. All reagents used in any chemical pretreatment must be purified, including those reagents used in making up standard mixtures for calibration purposes. Mitchell (1948) gives an excellent account of the application of spectrochemical methods in biological work.

Diagnosis and Control

The second problem in trace-element studies is concerned with methods of diagnosis and control of plant and animal diseases associated with deficiencies. Such methods are of immense economic importance.

There are three methods of diagnosis. In the first method, deficiencies are recognized by specific symptoms exhibited by

water and nutrient salts used in preparing the culture solutions, and by solution from containing vessels. There also existed the possibility of atmospheric contamination. The same problem was presented in the study of animal nutrition, the main difficulty in obtaining proof of the essential nature of an element depending on the availability of synthetic animal foods free from the elements concerned.

In order to investigate the essentiality of a particular trace element, means had to be devised of preventing the introduction of foreign material from all the possible contaminating sources. For example, so-called pure analytical reagents often contain amounts of trace contaminants (e.g., Fe impurity in Na_2CO_3) and these may be sufficient in themselves to supply the needs of the plant and animal. It is therefore imperative to stress the need for the purification of all material used in this type of work, as for example the purification of Na_2CO_3 used in plant ash fusions and the avoidance of metal parts in water distillation apparatus. In this connexion, while various plant and animal diseases have been attributed to particular deficiencies, the possibility of interaction between two or more elements must not be excluded. The purification of chemicals free from trace contaminants has been discussed by Stiles (1951) where references to the preparation of pure culture media are to be found, and a full account of the use of sand and water culture methods in the study of plant nutrition is given by Hewitt (1952).

Regarding the role of the trace elements in plant and animal metabolism, recent research would appear to indicate that their function is catalytic in nature and concerned with the regulation of normal growth processes.

Analytical Techniques

In investigating the part played by trace elements in plant and animal nutrition it is essential that methods for their quantitative determination be available. The concentration of these elements in plant and animal material is so low that the ordinary methods of chemical analysis are not sufficiently accurate. During the last twenty-five years a number of physical methods of

analysis have been developed for the measurement of minute quantities of material, and it is possible by means of these to estimate with reasonable accuracy most of the trace elements in plant and animal matter. Absorptiometric and spectrographic analytical methods have mainly been used. The absorptiometer is a form of colorimeter incorporating photoelectric cells by means of which the depth of colour of a solution is matched against that of a standard solution, and thereby measured. In the spectrograph a small sample of the material to be analysed is placed in an electric arc, flame, or other suitable source of excitation, in such a way that the molecules of the sample are dissociated into their constituent atoms, which are then stimulated to emit radiation. This radiation is limited to certain wavelengths characteristic of the elements in the substance and of the conditions of excitation employed. The radiation is passed through a prism and recorded as spectrum lines on a photographic plate. Each line possesses a density or intensity of blackening, which, under suitable conditions, is a function of the concentration of the element excited. The spectrograph affords the most sensitive method of measuring small quantities of a large number of elements simultaneously, and provides a permanent record, so that results are available for future reference. In the analysis of trace elements in plants, soils and related material, attention must be drawn to the need for freedom from contamination at all stages of the procedure. All reagents used in any chemical pretreatment must be purified, including those reagents used in making up standard mixtures for calibration purposes. Mitchell (1948) gives an excellent account of the application of spectrochemical methods in biological work.

Diagnosis and Control

The second problem in trace-element studies is concerned with methods of diagnosis and control of plant and animal diseases associated with deficiencies. Such methods are of immense economic importance.

There are three methods of diagnosis. In the first method, deficiencies are recognized by specific symptoms exhibited by

the plant or animal. In the plant, foliage symptoms are usually displayed, as for example the characteristic grey spots in the lower half of the oat leaf associated with manganese deficiency. In the animal, definite symptoms are recognized such as deformity of the leg bones in chicks fed on manganese-deficient diets. Good colour photographs of symptoms displayed by plants suffering from various mineral deficiencies are given by Wallace (1951). The second method by which deficiencies may be determined is provided by the methods of analysis referred to earlier. The results obtained would provide evidence of the adequacy or otherwise of the quantity of various elements in the plant or animal, but at present such information is limited. With regard to the plant, it would be necessary to establish the minimum quantities of the respective elements in the different plant organs for each species at different stages of development. At the present time there are few available data on the trace-element contents of the different animal organs, and mixed-herbage analyses are taken as an index of trace-element status in the animal; such analyses have little value however, unless sampling errors (especially on hill pastures) are taken into account. Calder (1955) has investigated the variation in trace-element content of hill pastures and has recommended a method for the sampling of hill soils and herbage for trace-element analysis. The normal variation in mineral content of mixed hill pastures was investigated with special reference to the trace elements manganese, cobalt, nickel, and iron. The variations in the cobalt and nickel contents of mixed pastures were found to be as great as those of acetic acid extracts of soil samples taken at the points where the pasture was sampled, and ranged from approximately 30–50 per cent. The variations in manganese and iron contents were somewhat less (20–30 per cent), while those in major-element (Ca, K, Mg) and silica-free-ash contents were less than 20 per cent, with the possible exception of magnesium for which the variation is slightly higher. Possible contributory factors to the normal variation in each case, namely (*a*) analytical error, (*b*) soil type and plant association, (*c*) seasonal effect, and (*d*) personal error in sampling, were examined. The analytical

1. Cocoa tree: a mature tree may attain a height of twenty to thirty feet but it is a common practice to prune the trees so as to facilitate harvesting the pods. (*Photo: P. B. Redmayne*)

2. Cocoa pods are opened by knocking against a large stone, or, as illustrated here, by splitting the husk with a cutlass. (*Photo: P. B. Redmayne*)
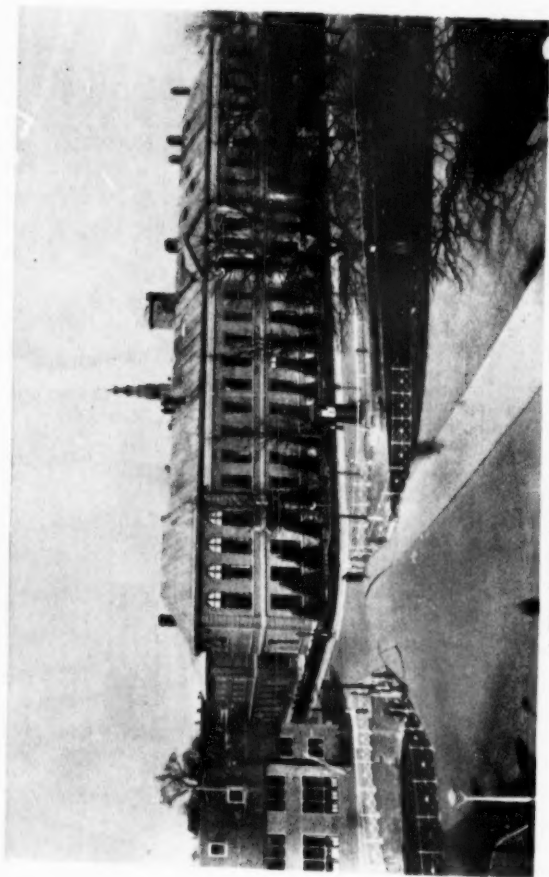
3. Building a fermenting heap on the ground: the heap is covered with leaves if there is a likelihood of rain. (*Photo: P. B. Redmayne*)
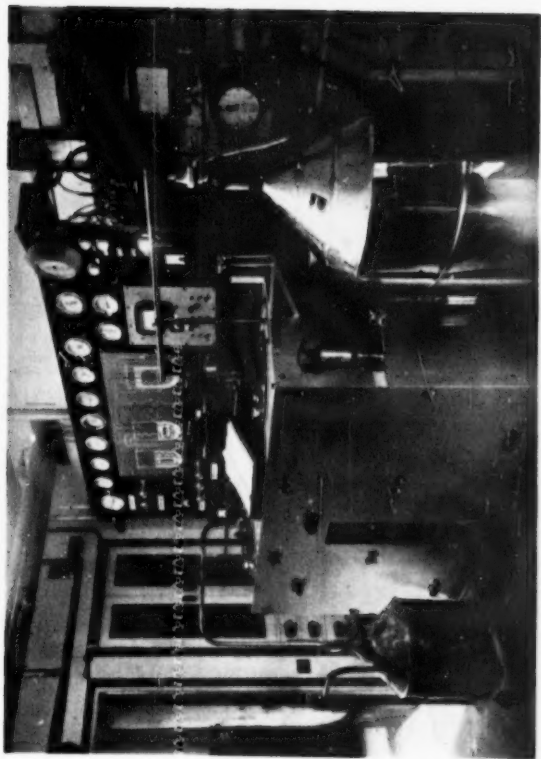

4. Beans being dried in the sun on trays. (*Photo: P. B. Redmayne*)

5. The Kamerlingh Onnes Laboratory, Leiden.

6. Helium Liquefier at the Clarendon Laboratory, Oxford.
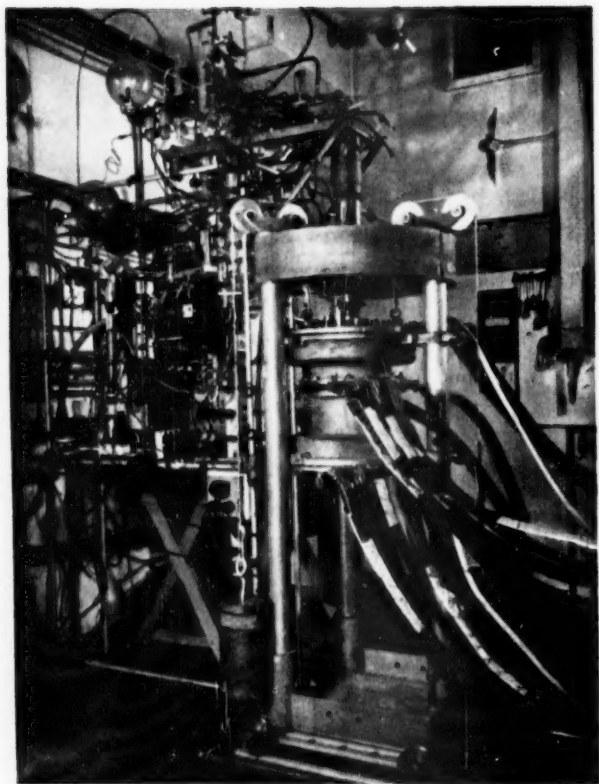
7. Apparatus for nuclear cooling. The water-cooled solenoid surrounding the cryostat produces the high magnetic field needed to align the atomic nuclei at $0 \cdot 01^\circ K$.
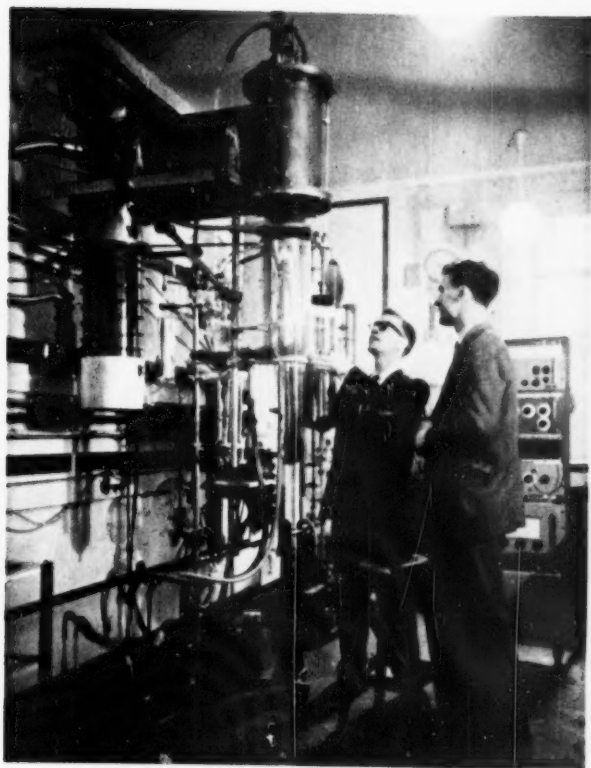
8. Helium cryostat for work down to $0.7°K$.
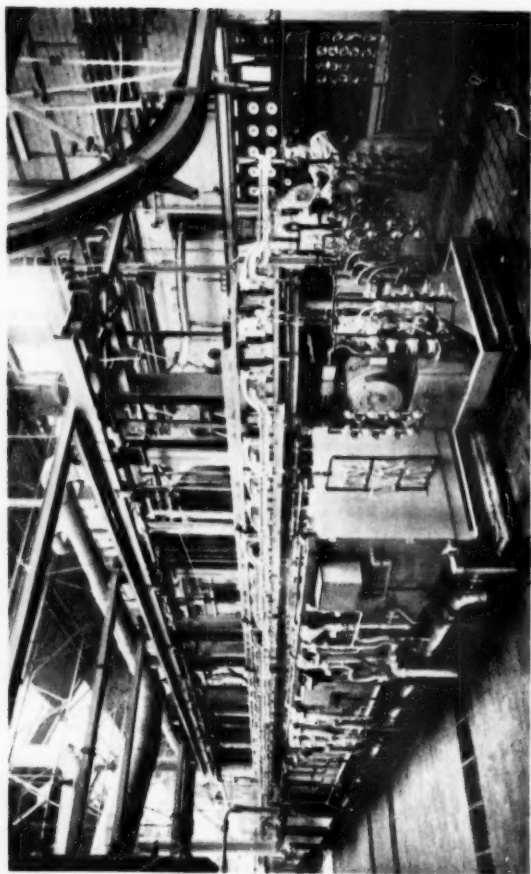
9. An automatic copper, nickel, and chromium plating machine for torch and cycle lamp cases. (*Courtesy of The Ever-Ready Co. (Great Britain) Ltd, and W. Canning and Co. Ltd.*)
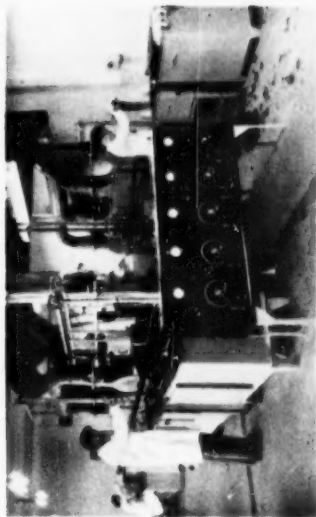
10. Well-equipped English electroplating laboratory where, under the best conditions, some of the problems described in the text are being investigated. (*Courtesy of Electrochemical Engineering Co. Ltd.*)
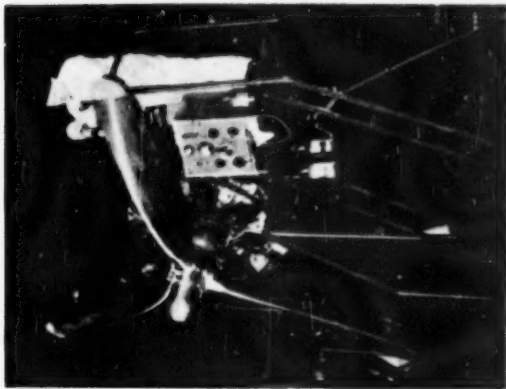
11. Repairing damaged electroplating on an aircraft propeller by the Dalic plating process. (*Courtesy of Metachemical Processes Ltd.*)
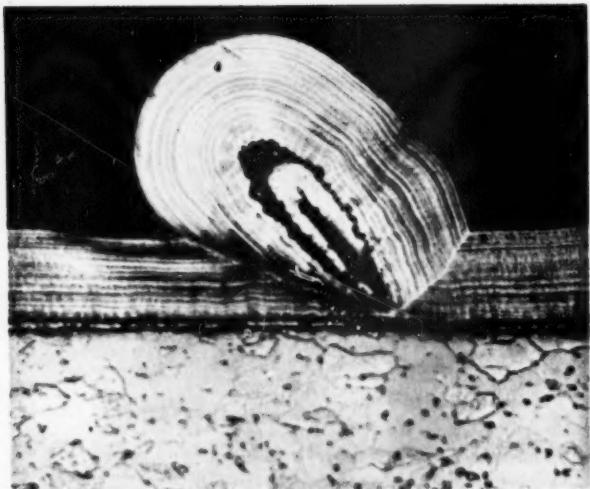
12. Section through a nodule in a bright nickel deposit. The laminated structure due to a periodicity in deposition is clearly shown: the nodule itself arose from a loose sliver of metal. (*Courtesy of The British Non-Ferrous Metals Research Association.*)
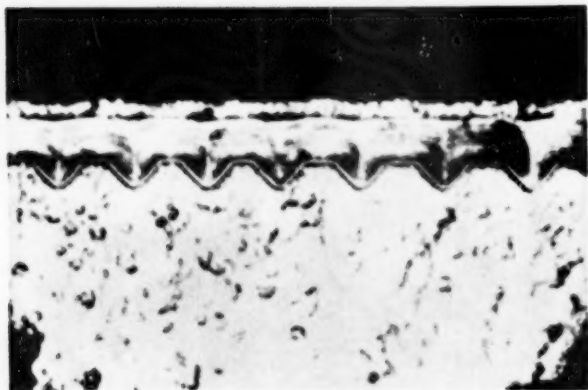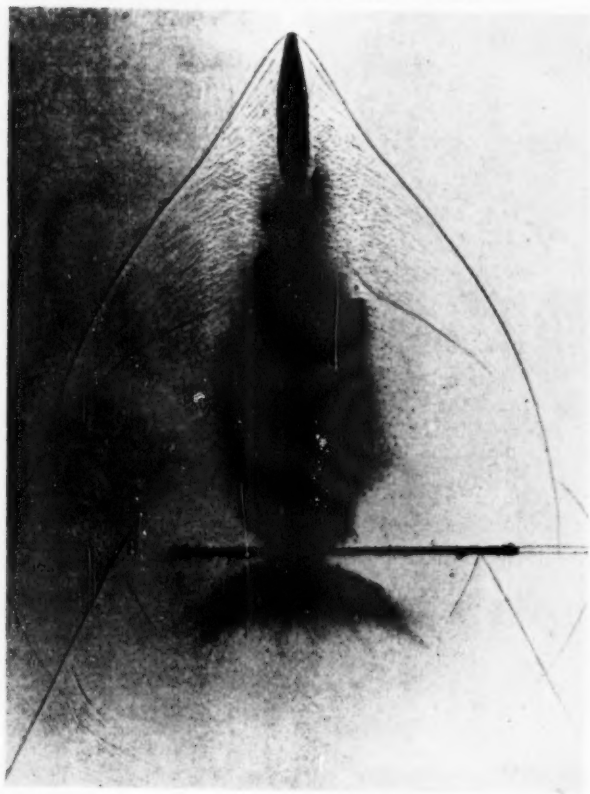

13. Bright nickel plate with exceptional levelling powers, deposited on a gramophone record master. (*Courtesy of Hansom-Van Winkle-Munning Co. (U.S.A.)*)
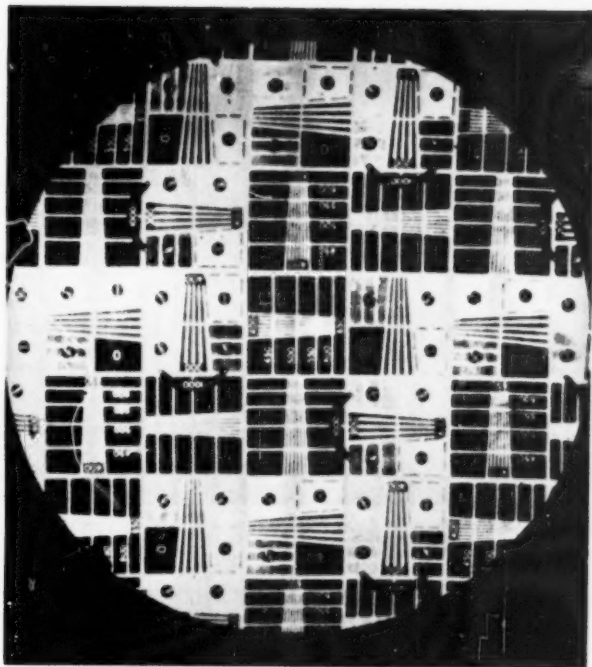
14. Demonstration illustrating the formation of a water spout and fine mist dispersion caused by intense ultrasonic cavitation at the surface of a column of water. (*Courtesy of Roto-Finish Ltd.*)
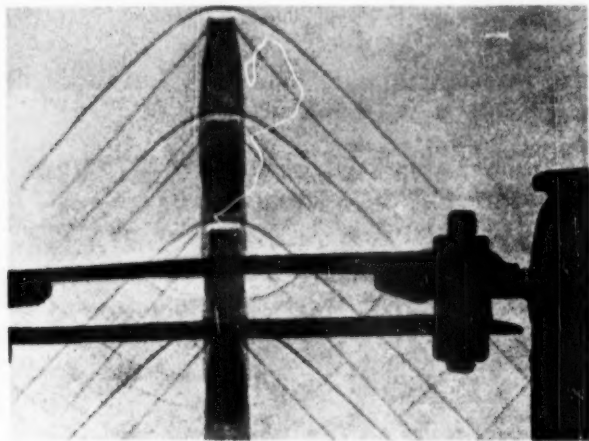
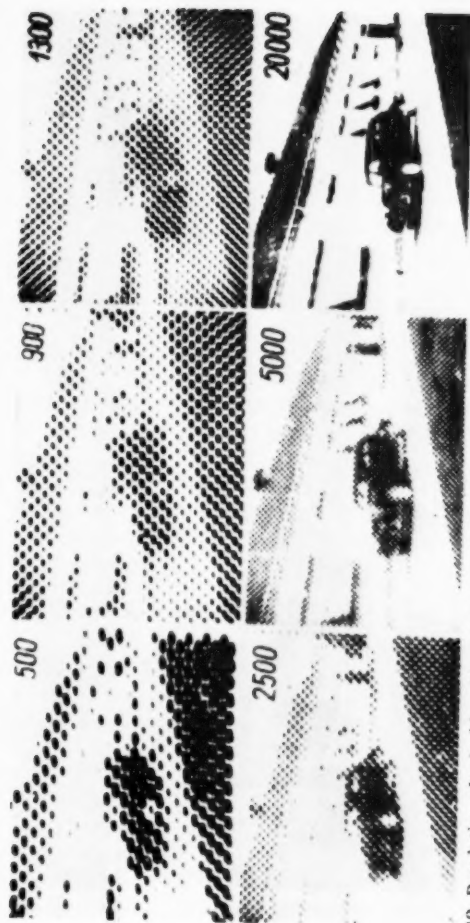15. Spark shadowgraph of a bullet in flight.

16. Resolution obtainable with an image converter tube.

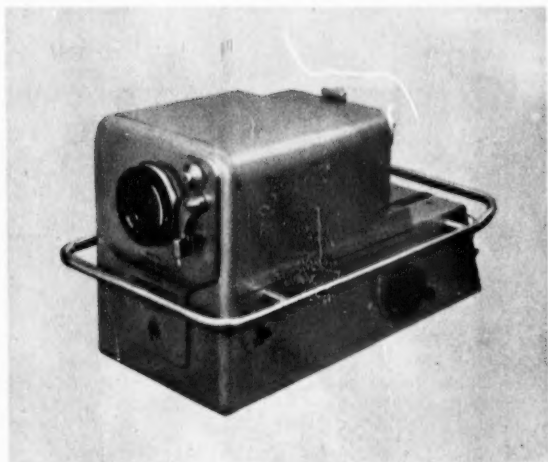17. Bullet travelling at 2,400 ft/sec. photographed with image converter equipment: exposure time 1µsec.
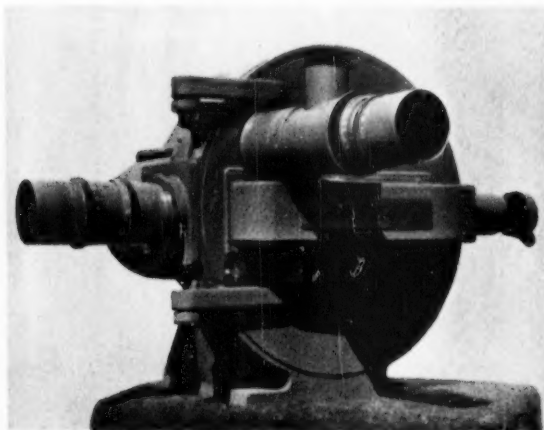

18. Multiple spark shadowgraphs of a bullet recorded on a single plate.

19. Resolution obtainable with various numbers of picture elements.

20. Image dissecting camera using lenticular plates. (*Courtesy of J. Langham Thompson Ltd.*)

21. High-speed continuous running 16mm. film camera.

and personal errors were shown to be relatively unimportant, and there was no seasonal effect. The variations were found to be generally of the same order of magnitude for areas uniform within themselves, but differing in vegetation and soil type. A fuller account of this work and the sampling of hill-lands for trace-element investigations is given by Calder and Voss (1957). A third method of diagnosis consists in introducing the element in a suitable form, e.g., as a solution, or as a soluble salt, into the plant or animal and observing the reaction. The principle underlying such methods is that the introduction of the element into the plant or animal in which the element is deficient will produce a response in the direction of a cure of the disease. These methods may further serve as methods of prevention and control of disease. In the plant a solution of the element is absorbed through a cut surface. The usual response is a colour change in the leaf which becomes greener and this may be accompanied by an increased rate of growth. The animal may be 'drenched' with a suitable soluble salt of the element, or the salt may be added to the diet and the reaction noted.

Methods of control in the plant involve (a) the application to the soil of a soluble salt of the element, e.g., copper sulphate in the control of copper deficiency, (b) spraying of the plants or crop, e.g., manganese sulphate spray for the correction of manganese deficiency in sugar beet and oats, (c) injection into the plant of a salt of the element, e.g., the injection of solid ferrous sulphate into the trunks of fruit trees affected by iron deficiency. In the animal effective measures of control include (a) dosage with pills or tablets, e.g., 'cobalt' pills in the control of cobalt deficiency in ruminants; the use of 'licks' and mixtures containing the necessary element, e.g., 'cobalt licks' in controlling cobalt deficiency, (b) the inclusion in the diet of a salt of the element concerned, e.g., the addition of manganese sulphate to the diet of chicks to prevent manganese deficiency, and (c) the spreading on the land of appropriate salts, e.g., the application of cobalt sulphate in instances of 'pining' disease of sheep, at the rate of 2 lb of the salt per acre, will raise the cobalt level of the pasture to a value suitable for carrying healthy stock.

C

The curative measures to be adopted are more involved when the problem is one of excess as opposed to deficiency. The problem may be further complicated when both deficiency and excess occur together, e.g., cobalt deficiency and molybdenum excess. One difficult problem centres round the inter-relationship of lime and trace elements. A trace-element deficiency may be due to (*a*) an absolute shortage of the element in the growth medium or (*b*) the inability of the plant to utilize what is present in the soil following the effects of lime in rendering certain compounds insoluble or unavailable, in other words lime-induced deficiency. In addition lime does not have the same effect on all trace elements. Cobalt, manganese, and lead are more soluble in acid than in alkaline media. Lime will therefore aggravate deficiencies of cobalt and manganese: if, however, there is an excess of lead in the soil, liming will reduce the solubility of the lead and hence the availability of lead to the plant. On the other hand molybdenum forms compounds more soluble in alkaline than acid media, and on a soil carrying an excess of molybdenum, liming will aggravate the difficulties.

The Role of the Elements

Reference has been made to the elements carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulphur, which form the organic constituents of plant and animal tissues, and the mineral elements calcium, potassium, magnesium (sometimes referred to as the major elements), and iron. The animal also requires sodium and chlorine. Silicon is included among those elements which produce beneficial effects on the growth of certain plants, but has not so far been shown to be absolutely essential to growth. Some plants, particularly cereals and grasses, grown in the absence of silicon seem to be susceptible to attack by fungi. The general functions of those elements in plant and animal nutrition are reasonably well understood. In the plant, carbon, hydrogen, and oxygen are derived from the air and water and used to build up fats and carbohydrates; nitrogen, phosphorus, and sulphur are obtained from the soil and combined with the first three to form proteins. The power of the plant to fix carbon

lies in its green pigment chlorophyll, which contains magnesium, while iron, although not a constituent of chlorophyll, is required for its formation. Calcium and potassium fulfil important functions in the cell sap. In the animal body, carbon, hydrogen, oxygen, and nitrogen are required combined in the form of fats or oils and proteins, which form the major part of the body tissues. It must also be noted that water is the most abundant substance in the animal body. Calcium and phosphorus are required for skeleton formation and are necessary constituents of other tissues. Sulphur is found in the tissues and is an essential part of sheep wool. Sodium and chlorine are required in relatively larger quantities. The exact role of sodium is not clear, although it is known to be essential to life, while chlorine is present in, and necessary for the formation of, acid in gastric juice. Potassium, though it must be present, is not so important an element to the animal as it is to the plant. Its functions are not yet completely understood, but are concerned with the regulation of muscular movements. Magnesium is required by the body in comparatively small amounts and is very important physiologically, being intimately associated with calcium metabolism. Iron exercises functions of fundamental importance; its association with anaemia and its concentration in the red corpuscles of the blood are well known.

The minor mineral constituents or trace elements in plant and animal matter occur in minute quantities; Calder (1955) reports major and trace-element contents in hill pastures from southeast Scotland of Ca 0·09–0·18 per cent, K 0·58–1·22 per cent, Mg 0·05–0·16 per cent, Mn 149–463 p.p.m., Co 0·04–0·30 p.p.m., Ni 0·52–9·34 p.p.m., and Fe 100–434 p.p.m. Those trace elements that have been shown to be essential mineral constituents of plants and animals are listed in Table I. Iron occurs in the animal body in such amounts that it is not generally considered as a trace element; nevertheless its action is bound up with them to such an extent that it may be regarded as occupying an intermediate position. In the table certain elements are placed in brackets, e.g. silicon among the major elements, and selenium, fluorine, and nickel among the trace elements. While silicon

produces beneficial effects on the growth of certain plants, there is no evidence to show that it is absolutely essential in either plant or animal nutrition. The trace elements selenium and fluorine occur in plants, but there is no definite evidence that they are essential in plant nutrition. On the other hand, an excess of selenium in plants is associated with disease of livestock feeding on them, while if fluorine be ingested by animals in amounts much larger than the usual traces it interferes seriously with bone metabolism. With regard to nickel, there is no evidence to show that it is essential for either plant or animal, and any importance attached to it is due rather to its poisonous effects on crops.

TABLE 1

The Mineral Constituents of Plants and Animals		
Category	Source	Mineral Constituents
MAJOR	Plant	Ca, K, Mg, (Si).
	Animal	Ca, K, Mg, (Si), Na, Cl.
TRACE	Plant	Mn, Cu, Zn, B, Mo, (Se), (F), (Ni).
	Animal	Mn, Cu, Zn, Co, I, (Ni).

(Fe, with arrows indicating range across major and trace categories)

In the following brief review of the essential trace constituents in plant and animal nutrition, the more important deficiency diseases attributable to trace-element shortages are discussed.

INDIVIDUAL TRACE ELEMENTS

Manganese

The agricultural significance of manganese was not realized until deficiency of the element was associated with the disease of oats called 'grey speck'. The disease is characterized by the appearance in the leaves of small chlorotic areas, which gradually expand, becoming brown at the margins and grey in the centre, eventually coalescing to form brown streaks due to the necrosis of the tissues in these specks. Two other well-known pathological conditions in plants are associated with manganese deficiency, viz., 'speckled yellows' of sugar beet (intravenal

chlorosis of the leaves) and 'marsh spot' of pea (necrosis of seed cotyledons). The use of manganese sprays is effective in controlling these deficiencies. A number of these diseases are due to the low availability and oxidized state of manganese under alkaline conditions in the soil.

With regard to animal nutrition, manganese-deficient rations have been shown to give rise to defective bone formation in birds, as for example in the disease of young chickens known as 'perosis' or 'slipped tendon'. This disease is characterized by a deformity of the leg bones and to some extent of the wing bones. The addition of 10 parts of manganese per million parts of food corrects this condition. On manganese-deficient diets egg production and hatchability are affected and embryos may be deformed.

Cobalt

Cobalt is not known to be necessary for normal plant metabolism, but the plant acts as carrier of the element to the animal for which it is essential. The function of cobalt is closely associated with blood formation and the bacterial flora of the ruminant stomach. It is required in the synthesis of vitamin B_{12}. Sheep and cattle depend upon this synthesis for their animal protein factor which contains vitamin B_{12}, and they cannot thrive without it. One feature of cobalt deficiency in the ruminant is a marked anaemia, and possibly the factors operating are (*a*) interference with the bacterial flora and synthesis of vitamin B_{12} and (*b*) the effect on blood formation. The symptom of cobalt deficiency in sheep is a loss of condition with scouring and is most characteristic. The condition can be corrected by the administration of cobalt at the rate of about 0·10 mg per sheep daily. Experience has also shown that a top dressing of 2 lb of cobalt sulphate per acre is most successful.

Two other diseases of cattle are known which respond to cobalt medication, viz., 'ketosis' or 'slow fever' (characterized by unpalatability and poor yield of milk) and 'malignant catarrh' (characterized by fever, cessation of rumination, and fall in milk yield).

Iron

Although iron is one of the most abundant elements in the soil it is often unavailable in sufficient quantity to satisfy plant requirements. While not a constituent of chlorophyll it is essential to its formation, so that the symptom of iron deficiency is a chlorosis due to lack of chlorophyll. Iron deficiency is a serious problem in fruit culture and certain timber trees also suffer from lack of iron. The presence of excess calcium carbonate in the soil, except when it is rich in organic matter, may render the iron unavailable. The deficiency is best controlled by the injection of iron salts into the trunks of the affected trees and recently promising results have been obtained by the use of chelating agents as a means of applying iron to plants (e.g., EDTA).

In the animal, iron deficiency is associated with anaemic disorders, as for example that developed sometimes in sucking pigs (piglet anaemia). The condition rarely occurs with litters having access to soil or pasture. Control is effected by early dosing with a solution of iron and copper salts. Copper is added here as it functions in the mobilization of iron for haemoglobin formation.

Copper

Copper deficiency in plants is characterized by a dieback of growing points and is sometimes accompanied by deformed growth. Two conditions of plants attributed to copper deficiency are (*a*) 'exanthema' or 'dieback' or chlorosis of fruit trees, and (*b*) a disease of plants known as 'reclamation disease' or 'exanthema' of citrus and other fruits.

In the animal it has been shown that copper protein compounds occur in the blood and liver of mammals. Although the actual part played by the compounds in the physiology of the animal is not clearly understood, the function of copper is apparently to be found partly in the role of these copper protein compounds. Copper deficiency results in the condition known as 'enzootic ataxia' or 'swayback' in sheep (general unthriftiness and retardation of growth). These conditions have been corrected by copper medication.

Zinc

Zinc deficiency in plants is associated with a number of disorders such as 'little leaf' and 'mottle leaf of citrus' (characterized by small narrow leaves). Zinc has never been shown to cause deficiency disease in livestock, but deficiency symptoms can be induced in laboratory animals on synthetic diets.

Boron

Boron is essential in plant nutrition but although present in the animal body there is no proof that it performs any useful function. Boron deficiency is fairly widespread throughout the world among fruits and vegetables. Deficiency conditions are associated with the following diseases: 'heart rot' of sugar beet and mangold; 'raan' of swede and turnip; 'cork' of apples. The deficiency is readily controlled by the application of borax to the soil usually in amounts varying between 25–50 lb/acre. Spraying is suitable for fruit trees.

Iodine

Iodine is an essential element in animal nutrition but is not regarded as necessary for the plant. Certain compounds, e.g., iodophenoxyacetic acid, have been investigated and found to be of value as plant growth substances. The results to date suggest that organic compounds of iodine may prove useful as plant growth substances. In the animal, iodine exchanges within the body are regulated by the thyroid gland which derives iodine from the food and utilizes it for the formation of thyroxine. The function of iodine in this form is concerned with physical and mental development, reproductive capacity and growth of wool and hair. In 'iodine-deficient' parts of the world or 'goitre' areas, goitre and hairlessness occur among livestock fed upon unsupplemented rations. The condition may be corrected by the addition of potassium iodide to the ration.

Molybdenum

Molybdenum has been shown to be needed for plant nutrition.

There is no evidence, however, that it is essential to animal health. Nevertheless, plants can take up molybdenum in amounts injurious to animals. One example is provided by the 'teart' pastures in Somerset where a relatively high molybdenum content of 'teart' herbage (3–20 p.p.m.) causes scouring of grazing ruminants. The malady is cured by the feeding of copper sulphate. A high intake of molybdenum apparently reduces the concentration of copper that can be stored in the liver.

Selenium, Fluorine, and Nickel

All three elements are known to occur in plants, but there is no evidence that they have any essential role. Cases of 'selenosis' (Eire) and fluorosis in cattle have been reported. Crops containing up to 50 p.p.m. nickel have been grown on soil on which cereals have displayed symptoms of heavy metal chlorosis.

REFERENCES

Calder, A. B.: *A study of the variation in trace-element content of hill pastures.* (Thesis: University of Edinburgh, 1955.)

Calder, A. B., and Voss, R. C.: *The sampling of hill soils and herbage, with particular reference to the determination of the trace elements.* (Consultative Committee for Development of Spectrographic Work. Bulletin 1, 1957.)

Hewitt, E. J.: *Sand and water culture methods used in the study of plant nutrition.* (Commonwealth Bureau of Horticulture and Plantation Crops. Tech. Comm. No. 22, 1952.)

Mitchell, R. L.: *The spectrographic analysis of soils, plants and related materials.* (Commonwealth Bureau of Soil Science. Tech. Comm. No. 44, 1948.)

Stiles, W.: *Trace elements in plants and animals.* (Cambridge Univ. Press, 1951.)

Wallace, T., 1951: *The diagnosis of mineral deficiencies in plants by visual symptoms.* (London, H.M.S.O.)

HIGH-SPEED PHOTOGRAPHY

A. M. P. BROOKES

HIGH-SPEED photography may be said to begin when the limit on the shutter speed of everyday cameras is passed: this means at about one-thousandth of a second. Even quite modest conventional cameras have between-lens shutters speeded up to a five-hundredth of a second, and the majority of focal-plane shutters will give a genuine one-thousandth, so here we shall confine our attention mainly to exposure times shorter than this.

In essence, the problem of photographing an object in a very short time is a straightforward one involving only a suitable intensity of illumination and some method of limiting the time the image of the object being photographed remains on the sensitive surface of the recording material. But as desired exposure times get shorter so the techniques and apparatus required become, in general, more elaborate.

The simplest type of high-speed camera is the drum camera illustrated in Figure 1. It consists of a drum about 30 cm in diameter carrying a strip of photographic film round its periphery, which can be rotated so as to give the film a maximum linear velocity of 300 ft/sec or so. The drum is enclosed in a light-proof container and the film moves behind a narrow slit transverse to its motion. An image of the object is projected upon the slit which thus masks off all but a narrow portion of this image. The lens used with this apparatus is fitted with a conventional type of shutter which is arranged to remain open for the time of one revolution of the drum, thus giving a streak record of the component, in the direction of the slit, of any motion the object may have had during the time the lens shutter was open. There is thus no 'picture' of the object in the generally accepted sense of the word but, nevertheless, a great deal of useful information about the object's motion can be obtained
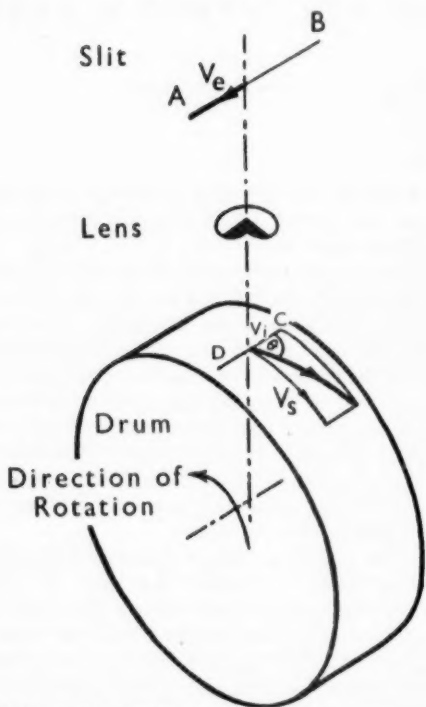
Fig. 1. Diagram of a simple drum camera. From measurements of
the streak record, velocities of movement of the object can be
determined relative to the speed of movement of the film. (*Courtesy of the* Photographic Journal.)

from this simple arrangement. The slit can be made very narrow
and variations in position of the object occurring only 0.25×10^{-6} sec apart in time can be recorded using a conventional $f\,1.9$
lens and sufficiently bright illumination. This type of camera is
also very useful where the relation between brightness and time

for a self-luminous object, such as an explosive charge, is required.

When a conventional photograph is required the most straightforward method is to use a normal camera set with its shutter open in a darkened room and to illuminate the object only for the exposure time required. This can be done by means of a foil-filled flash bulb, giving an exposure time of a few milliseconds (seconds $\times 10^{-3}$), but for really high speeds it is necessary to use an electronic flash tube, or an electric spark. Electronic flash tubes contain a gas, such as xenon, at low pressure and a rapid discharge between two electrodes in the gas is obtained when a sufficiently high voltage is applied to the tube, being a triggering potential applied to a third electrode. Tubes of this type can be arranged to give out all their useful light in as short a time as 2 microseconds (seconds $\times 10^{-6}$) although this time can be extended to 1 millisecond if necessary by suitable modification of the tube and control circuits.

A simple spark discharge in air will give a briefer exposure still, an exposure much less than 1 microsecond, although the total amount of light available is lower than that from a flash tube. For many purposes, such as the silhouette of a bullet in flight (Inset 15), the light output is quite sufficient, and the smallness of the source makes it possible to arrange the illumination in an efficient manner so that the shock waves and turbulence in the air caused by the bullet are clearly seen. Very roughly, if the energy to be dissipated in a discharge tube or spark is N joules, the effective exposure time can be kept as small as $N \times 10^{-7}$ for values of N in the range of 10^{-1} to 10^4, and discharge efficiency in the range of $10 - 100$ lumens/watt. This implies that a luminous flux from a single flash or spark source is rarely in excess of 10^9 lumens and is a fundamental limitation of this method.

Recently a source depending on the passage of a shock wave through argon has been developed and this gives a flash as brief as 0·25 microsecond.

It is not always possible to perform an experiment in the dark and thus limitation of exposure by some type of shutter becomes

necessary. Conventional mechanical shutters being much too slow, considerable thought has been given to shutters operated entirely electrically. The oldest of these is the Kerr cell, which depends for its operation on the fact that the plane of polarization of light passing through a glass-walled cell containing nitrobenzene is rotated when a high potential is applied between electrodes inserted in the cell. Thus if two polarizing filters are placed one on either side of the cell and are orientated so that no light passes, then, on the application of the appropriate potential to the electrodes the polarizing filters are effectively uncrossed so as to permit the passage of light while the potential on the electrodes is maintained. It is possible to produce appropriate voltage pulses of very short duration and exposures as short as 10^{-8} sec can be obtained in this way.

A more recent electrical device that can be used as a shutter is the image converter tube.[*] The tube, illustrated in Figure 2, consists of a plane photo-cathode at one end of which the object to be observed is imaged optically, and a fluorescent screen at the other end on which the electrons emitted from the photo-cathode are focused to give a fluorescent image (Inset 16). The arrival of the electrons at the fluorescent screen depends on the application of an electric field which can be pulsed in the same way as for the Kerr cell so that the time during which the electron image is projected may be made very short, even down to 3×10^{-9} sec. The image on the screen is then recorded photographically (Inset 17). An advantage over the Kerr cell is that image intensification can be achieved with the image converter, whereas there is an inevitable loss of light due to absorption in the Kerr cell.

All these devices require, of course, to be triggered at just the right moment and achievement of reliable triggering is often the most difficult part of the operation. With the foil-filled flash bulb there is a delay of several milliseconds before useful light is emitted and, in general, there is always some delay between the initiating signal and the firing of the flash or operation of the shutter in all systems, although this delay may be very small.
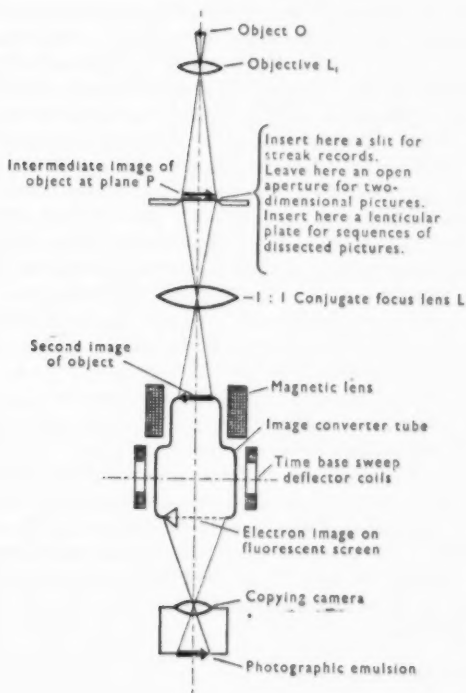
[*] *Science News*, **40** 19.

Fig. 2. Schematic diagram of image converter tube apparatus with an intermediate image plane at P. If a slit is placed at P this apparatus can be used for streak records. If an open aperture is left at P the apparatus can take ordinary two-dimensional pictures of very short exposure. If a lenticular plate is placed at P the image at the photo-cathode is dissected into small dot elements. If a time sweep is then applied to the tube the composite dissected picture sequence appears on the fluorescent screen and can be recorded by a plate camera. The individual pictures of the sequence can subsequently be unscrambled. (*Courtesy of Butterworth's Scientific Publications.*)

It is important, however, that it is as constant as possible so that due allowance may be made for it although, of course, if it is long it may not be possible to obtain a firing signal sufficiently far in advance. Thus, if one wished to photograph a projectile moving at 2,000 ft/sec, it might be most inconvenient to have to arrange a trigger to operate some 20 milliseconds before the projectile came into the camera field since this would be equivalent to a distance of 40 ft. There are occasions also when the event being photographed will not occur at a time that can be forecast with any accuracy, and in these cases a system having the minimum of triggering delay time is essential so that the start of the event can be used to operate the camera. If this is not possible then a series of pictures must be taken to cover the whole of the time during which it can be forecast with certainty that the event will take place.

It thus becomes necessary to be able to take what may be regarded as high-speed cinematograph pictures to make sure of getting the one or two pictures that are important, although there is often a considerable difference between the techniques necessary to produce a series of pictures which will, when projected, give an illusion of motion and a similar series which will be suitable for observing one by one. In the former case blurring in each individual frame is of no consequence, whereas in the latter case the maximum possible sharpness in each picture is usually desirable.

High-speed cinematography

In many instances exactly the same methods and apparatus can be employed as for single pictures except that the light source or shutter is operated several times in succession to give multiple images (Inset 18) on the same photographic plate. This type of picture is very easy to assess since the plate is known to have been motionless and all relative displacements between successive exposures can readily be measured. It is not practicable, however, to get more than a dozen or so exposures without confusion arising and it may then be necessary to place successive images on fresh parts of the sensitive material. Here again

conventional methods of ciné photography become unsuitable or impossible with increase of the number of frames/sec required. Intermittent film motion cannot be achieved much above 300 frames/sec and beyond this the film is arranged to run at a steady speed, the image being caused to follow the motion of the film during the time of exposure by some optical method employing rotating prisms or mirrors (Figure 3). A limit is again reached when the film speed is about 250 ft/sec, which makes it possible to take 16 mm standard pictures at about 10,000/sec or half the usual frame height at 20,000/sec. If it is required that each individual picture shall be sharp, then the exposure time for each frame must be quite a small fraction of the framing rate. (Inset 21.)

It is also possible to dispense with optical compensation for the relative movement of film and image if a sufficiently short illumination time is attainable consistent with the maximum permissible blur. Using repetitive spark illumination and assuming that a blur of 1/200 of the frame height is permitted, it is possible to take pictures at a framing rate of 5,000 per second. For this type of camera the film can conveniently be mounted on a drum if the number of pictures desired does not exceed about 150. In this way the film can be run up to the required speed some time before the pictures are to be recorded, thus obviating the considerable wastage of film that is inevitable when accelerating the mechanism necessary to run a film from one spool to another at high speed. There is also no stress on the film and hence no danger of it breaking.

When it becomes impossible to increase the linear speed of the film a different method can be used in which the image to be recorded is swept optically over a stationary film on the inside of a drum. It is possible to give the rotating mirror which directs the image on to the film a much higher angular velocity than a drum because the mirror can be made very much less in diameter and 10,000 revolutions per second or more can be achieved. A series of 96 pictures at a framing rate of 15×10^6 pictures per second has been taken with this type of apparatus, the object being intensely self-luminous.
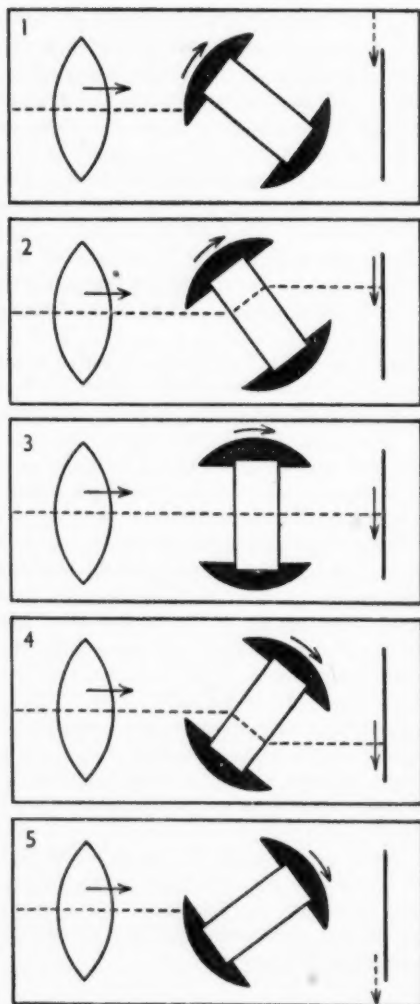
Fig. 3. Diagram showing the principle of image compensation by means of a rotating block of glass. (*Courtesy of J. S. Courtenay Pratt.*)

Image Splitting

Quite a different approach to the problem of producing a series of pictures at a high framing rate is the image splitting technique. The underlying principle of this is the possibility of combining several pictures on one photographic plate by a masking process so that any one picture is recorded as an array of dots, much as a half-tone reproduction of a photograph is produced for printing purposes, except that the aggregate area of the dots composing one individual picture is only a small fraction of the total area of the plate. The dots comprising one frame are therefore widely spaced from their neighbours, thus leaving room for several arrays of dots, representing successive frames, to be inserted between. If one imagines a photographic plate covered with dots in this manner it can be seen that, to view any one set of dots, a mask with holes corresponding to the dots we wish to see should be held in contact with the plate and the assembly viewed against a uniform source of illumination. A small displacement of the mask will bring another set of dots into view and this can be continued until all the sets of dots have been observed.

If a sufficiently small interval between adjacent dots comprising any one frame is chosen, the quality of definition of the picture as viewed can be made quite high (Inset 19) and similar to that produced on a television set, and if the dots themselves are made sufficiently small up to 300 separate frames can be recorded on a single plate. The great advantage of this system is that it involves only a very small change of image position from frame to frame which much facilitates the rapidity of framing that is possible. It is also extremely economical in material and will produce frames of very much greater linear dimensions than those of 8 mm or 16 mm ciné film.

It is not a practical proposition to move a physical mask close to the emulsion surface in the required manner and, in one design of this camera (Inset 20), the effect of moving a mask is achieved optically. In front of the sensitive surface of the photographic plate (Figure 4) there are placed two plates having regular
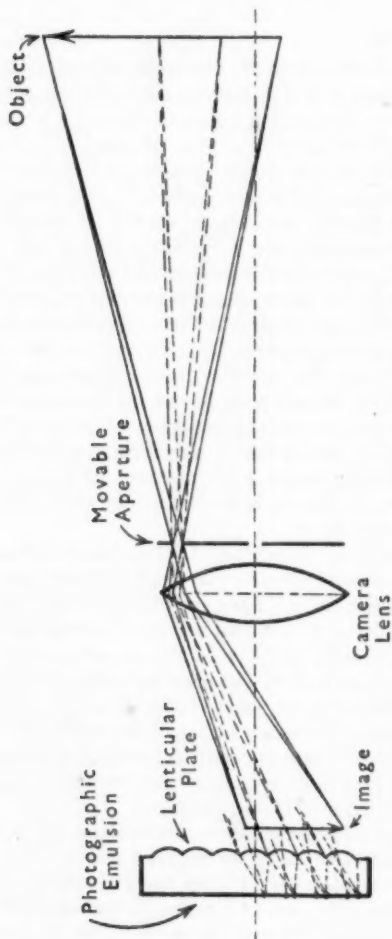
Fig. 4. Optical system of a series of high speed multiple frame cameras using lenticular plates for dissecting the image into dots. (*Courtesy of Engineering.*)

cylindrical lenticules on one surface of each. The pitch of the lenticules is 0·04 cm and the direction of those on one plate is at right-angles to those on the other. If, in addition, the plates are arranged so that the lenticular faces are touching, then the pair of plates is equivalent optically to a large array of small spherical lenses.

This plate-pair is mounted at such a distance in front of the photographic emulsion that images of a standard camera lens, mounted in its normal position relative to the photographic plate, are thrown by each small lens upon the emulsion surface. The aperture of the camera lens and the focal length of the small lenses are chosen so that the projected images are just touching one another and the plate is covered as efficiently as possible. Now if a disc having a series of small holes arranged in a spiral, a Nipkow disc, is rotated in front of the main lens in a plane at right angles to its axis, and if the spacing of the holes is such that only one hole at a time is in front of the lens, then behind each of the small lenses there will be an image of the small hole traversing the area covered by any particular small lens, and this will be the same for all the small lenses. Thus at any moment the image being projected upon the photographic plate will consists of an array of small dots, one for each of the small lenses, and there will be 625 of these for every sq.cm of surface of the photographic plate. Rotation of the Nipkow disc will effectively scan all the areas behind the small lenses and since the disc can carry two or more spirals in angular succession, the whole area of the plate can be scanned two or more times per revolution. On the assumption that a picture point is the size of the projected image of the hole in the Nipkow disc and that one set of picture points gives one frame, then, when a picture point has moved transversely by its own diameter, a second frame has been recorded. In this way any desired framing rate up to 250,000 per second with a picture resolution of 250×300 lines and with a sequence of 300 frames can be achieved. The effective aperture of the whole system is about $f\,6$.

When the series of pictures has been taken it is necessary to unscramble the result, and this is done by inserting the developed

plate into the camera again and viewing it by means of illumination projected through the whole optical system, thus masking all but the dots required for any particular frame. Slow rotation of the Nipkow disc will give a moving picture effect at a speed which is slower than the original event by a factor equal to the ratio between the taking speed of the disc and the viewing speed.

The lenticular plate and Nipkow disc method is only one of several methods of image dissection, but the basic principle is always the same in that the series of pictures is in some way chopped up so that displacement of image relative to sensitive material from frame to frame is kept at a minimum.

These limitations on the distance it is possible to displace an image in a given time do not apply in nearly such a restricting manner to the images produced with an image converter tube. Here the electrons forming the image can be given large transverse displacements by means of a magnetic or electrostatic field in a very short space of time, and thus a series of pictures can be displayed on the image converter screen at a very high framing rate. The limitation here is the size of the screen and the lowest acceptable quality of an individual picture, but a series of 16 pictures can be readily obtained with a resolution on the screen surface of 30 line pairs per millimetre all over a screen of 10 cm diameter. This resolution is better than that of many lenses used to produce the primary image on the photocathode.

Recently the techniques of image dissection and the image converter tube have been combined by the construction of a dissected cathode in the tube. This cathode consists of 0·001 in. squares of photosensitive material at 0·010 in. spacing. This will produce a similar dissected image on the fluorescent screen which can be swept across the available space between image elements so as to produce a composite record as with the lenticular plate and Nipkow disc method, only at a much higher framing rate. This rate is already as high as 5×10^7 per second for 50 frames and could well be extended to 10^9 per second or even faster. The main disadvantage is that only about one per cent of the total incident light is used to release electrons from the photosensitive surface because the latter is so sparsely covered

with sensitive material, but it is possible that suitable optical arrangement could improve this considerably and experiments are being carried out using lenticular plates for this purpose. The inherent possibilities of schemes of this sort seem to be very great and may well result in a very compact electronic camera capable of taking photographs at all speeds from stills to a series at a rate of a thousand million a second.

THE THYROID GLAND AND
IODINE METABOLISM

C. E. SEARLE

JUST over three centuries ago, in 1656, a London physician
named Thomas Wharton published the first accurate description
and illustration of the thyroid gland in a treatise on the glands of
the body called *Adenographia: sive glandularum totius corporis
descripto*. He also gave the gland the name 'thyroid' which is
derived from Greek and means 'shield-shaped'. Similarly the
German name *Schilddrüse* means shield-gland.

The gland is situated on either side of, and a little below, the
larynx, and consists of a lobe on either side joined by an isthmus
across the trachea. The weight of the thyroid varies consider-
ably, but an average figure would be nearly an ounce for a
normal man and rather more for a woman.

Wharton seems to have regarded the function of the thyroid
gland as being at least partly cosmetic, for he says that 'it con-
tributes much to the rotundity and beauty of the neck, filling up
the vacant spaces round the larynx and making its protuberant
parts almost to subside, and become smooth, particularly in
females, to whom for this reason a larger gland has been
assigned, which renders their necks more even and beautiful'.
However, he also suggested that the jelly-like material now
known as colloid, which can be expressed from the gland, serves
to lubricate the trachea. Other writers thought the thyroid might
act as a shunt for excess blood to protect the brain, or that it
forms a part of the vocal apparatus.

Around the middle of the nineteenth century it seems to have
been thought that the thyroid gland, at least in adults, had no
particular function, until it was found that surgical removal of
enlarged human thyroid glands produced in the patient a state

resembling the known diseases of myxoedema and cretinism, of which more will be said later. Animal experiments gave similar results, which were, however, often confused by the simultaneous removal of the adjacent parathyroid glands, which are vital to the calcium metabolism of the body.

The thyroid is now known to be one of the body's endocrine, or ductless, glands, producing a secretion that is liberated directly into the bloodstream. This secretion, the thyroid hormone, is released in amounts fitted to the body's requirements, a process apparently controlled by other hormones produced by the pituitary gland at the base of the brain.

NORMAL THYROID CHEMISTRY

The first clue to the remarkable chemistry of the thyroid gland came in 1895, when the German chemist Baumann found that it contained a high concentration of the element iodine, although it should be said that iodine deficiency had been suspected as a cause of human goitre soon after the first preparation of the element from seaweed ash in 1811. A normal thyroid contains approximately 10 milligrams of iodine, which represents about $1/2500$ of its total weight. The thyroid hormone itself is in fact an organic iodine-containing substance which is elaborated in the gland from tyrosine, one of the constituent amino-acids of the thyroid protein, and iodine which is obtained from the food and drinking water by way of the bloodstream.

The remarkable aspect of the thyroid's function, however, is not so much the actual synthesis of the hormone as the initial extraction of the traces of iodine circulating in the blood as the negatively-charged iodine ion, I^{-1}. The subsequent steps leading to the iodinated amino-acids can occur to some extent in other parts of the body, and can also be simulated in purely chemical experiments.

The two main iodinated amino-acids of the thyroid protein have long been known. They are $3:5$-di-iodotyrosine and $3:5:3':5'$-tetra-iodothyronine, or thyroxine as it is usually called. For a long time thyroxine, either alone or combined with other amino-acids in a peptide or protein, was regarded as

the only thyroid hormone. It was first isolated in America in 1916 by Kendall who succeeded in isolating 33 grams (1·25 oz) from three tons of ox thyroid gland. Its molecular formula is $C_{15}H_{11}O_4NI_4$, and this very high proportion of iodine (65 per cent) caused analytical difficulties which led at first to incorrect structures being proposed for the compound. It remained for Harington (now Sir Charles Harington, Director of the National Institute for Medical Research at Mill Hill, London) working at University College Hospital Medical School in London to deduce the correct structural formula in 1926, and the first successful synthesis of thyroxine was announced by Harington and Barger the following year. More recent syntheses now allow it to be manufactured on a large scale.

Mechanism of thyroid hormone synthesis

After the initial abstraction of the iodide ion from the blood by some mechanism that has not yet been clarified, the synthesis of thyroxine can be visualized as taking place in a number of stages.

The iodide is first oxidized enzymatically to elementary iodine. In this state it reacts with tyrosine, which besides having the characteristic amino-acid grouping $-CH(NH_2).COOH$ is also a phenol, capable of being iodinated in the benzene ring at the two vacant positions adjacent to the $-OH$ group. The resulting 3 : 5-di-iodotyrosine then undergoes a complex reaction (which can also be carried out chemically under oxidizing conditions) in which two molecules of di-iodotyrosine link to form one molecule of thyroxine; the three-carbon side-chain of one of the original molecules is eliminated in the process. See Figure 1.

The jelly-like colloid referred to earlier is actually the thyroid storage protein, thyroglobulin, of which the iodinated and other amino-acids are constituents linked through their amino- and carboxyl-groups. In the diagrammatic representation of a small part of one chain, R, R', and R″ represent various groupings varying from $-H$ in glycine, the simplest amino-acid, to $-C_{15}H_7O_2I_4$ in thyroxine (Figure 2). The protein is broken down to liberate thyroxine into the circulation as required.
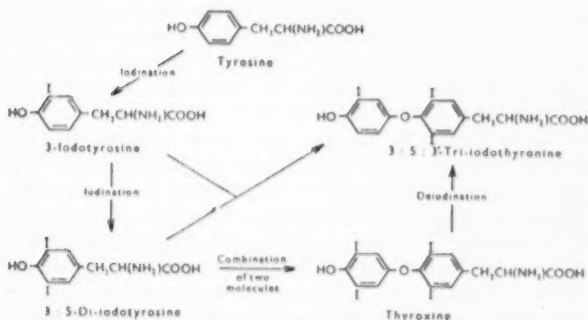
Fig. 1. Formation of thyroxine and tri-iodothyronine.

A major development in thyroid chemistry occurred in 1952 when Gross and Pitt-Rivers at the National Institute of Medical Research in London, and Roche, Lissitzky, and Michel in Paris, independently announced the isolation of another iodinated amino-acid present in the thyroid and in blood plasma, and its identification as 3 : 5 : 3'-tri-iodothyronine (that is, thyroxine less one of the two iodine atoms adjacent to the phenolic —OH group).
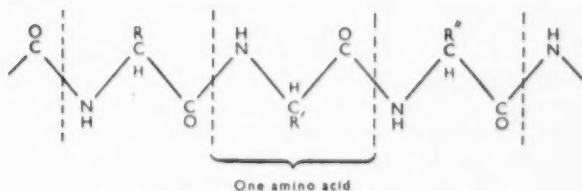

One amino acid

Fig. 2. Fragment of a protein chain.

Various biological tests in mammals soon showed tri-iodothyronine actually to possess several times the thyroid hormone activity of thyroxine itself. This unexpected result suggested that it, not thyroxine, might be the true active principle of the thyroid

gland, being formed in a further step by the enzymic removal of one atom of iodine from thyroxine. This would help to explain the puzzling time-lag of up to two days before injected thyroxine shows its effects in the body, and its long period of action.

The techniques that led to the discovery of tri-iodothyronine have also shown other iodinated compounds to be present in the thyroid. These include 3-iodotyrosine (1948) and $3:3':5'$-tri-iodothyronine (1955), and it will be clear that the two tri-iodothyronines could arise not only by de-iodination of thyroxine, but by combination of one molecule each of mono- and di-iodotyrosine by the mechanism already given for the synthesis of thyroxine. The evidence now indicates that $3:5:3'$-tri-iodothyronine is indeed formed by this mechanism in the thyroid, but by de-iodination of thyroxine in other parts of the body.

A further change, this time involving the amino-acid portion of the molecule, may be necessary, for experiments in rats without thyroid glands have shown that tri-iodothyronine is converted to the corresponding thyroacetic acid. This involves a change in the side-chain of the molecule from $-CH_2.CH.(NH_2).COOH$ to $-CH_2COOH$. It is at any rate suggestive that the acetic acid derivatives of both thyroxine and tri-iodothyronine have been found to stimulate respiration in surviving slices of tissue very rapidly, whereas the amino-acids themselves only do so after a considerable time-lag.

EFFECTS OF THYROID HORMONE

The administration of thyroid gland, a thyroid extract, or thyroxine to an animal produces wide and varied effects, all oxidative metabolic processes involving carbohydrates, fats, and proteins being accelerated. This acceleration is seen, for example, as an increase in the rate of heart beat, heat production, oxygen consumption, and urea excretion. However, it has long proved difficult to investigate these metabolic effects outside the living animal, and hence we have very little information about the detailed mechanism of hormone action and its importance in life processes. The observations on the thyroacetic acids just referred to may help us to understand these processes better, but

it seems premature to discuss various theories at this stage. Whatever the intermediate processes may be, much of the iodine is split off the molecule, to be excreted or to re-enter the metabolic cycle, while some of the hormone appears in the bile in a conjugated or degraded form.

An interesting aspect of thyroid hormone function is its importance in the process of metamorphosis in amphibians. When fed thyroid, tadpoles undergo metamorphosis prematurely into tiny frogs which do not, however, survive very long. Conversely, hormone deprivation results in the tadpoles continuing to grow without undergoing metamorphosis. Apart from its academic interest, tadpole metamorphosis provides one means of testing substances for thyroid hormone activity. A Mexican salamander known as the axolotl normally lives and breeds in the larval state, somewhat resembling a large, partially metamorphosed tadpole with four legs and a long tail. It can be made to complete metamorphosis by feeding thyroid.

DISORDERS OF THE THYROID

The main diseases to which the thyroid is subject, excluding those involving inflammatory or cancerous conditions, can be broadly divided into two groups – *hypothyroidism*, in which thyroid function is reduced or absent, and *hyperthyroidism*, in which the body suffers from an excessive formation of thyroid hormone. The state when there are no obvious signs of thyroid derangement is often called euthyroidism.

Hypothyroidism

In adults the effects of deprivation of thyroid hormone are seen in cases of *myxoedema*, a condition which arises when the thyroid atrophies and ceases to function. All the body's metabolic processes are slowed, and the sufferer is lethargic, mentally dull, and abnormally sensitive to cold. The name myxoedema refers to characteristic thickenings that occur around the face and hands, due to the accumulation of a gelatinous substance under the skin.

Once recognized, myxoedema can then be controlled by

administration of a thyroid preparation or synthetic thyroxine, with due precautions against overdosage. Prolonged treatment is necessary. The first recorded cure, now a classic case, was of a forty-six-year-old woman who was in an advanced stage of the disease in 1891. She was restored by G. H. Murray to normal life by treatment with thyroid extract, at first by injection and later orally, and lived a further twenty-eight years.

Obviously an essential prerequisite of an adequate supply of thyroid hormone is an adequate supply of iodine. If this is insufficient, the thyroid undergoes cellular enlargement and multiplication (*hyperplasia*), the extent of which depends on the seriousness of the deficiency. If the resulting enlargement of the gland makes it visible as a swelling in the neck it is known as a *goitre*.

These changes at first increase the gland's efficiency at trapping and utilizing the available iodine, and a balance may be reached so that the body still gets sufficient hormone for its needs, and signs of hypothyroidism do not appear. With a continued and severe iodine deficiency, however, the enlarged gland becomes incapable of meeting the strain and undergoes degeneration; a myxoedematous state then results.

Adolescence, pregnancy, and lactation impose a raised hormone demand on the thyroid, which sometimes undergoes a temporary enlargement at such times, even when the iodine supply is normally adequate.

The fact that even the apparently modest requirement of iodine, roughly 100–200 millionths of a gram per day for an adult human, is not met over large areas of the world's surface is responsible for the widespread occurrence of goitre as an endemic disease. Unlike most diseases goitre shows no preference for any particular race or area of the world, and there is hardly a country that can claim to be entirely free of it. A recent estimate gives the number of goitrous people in the world as approaching 200,000,000, and even in the last few years surveys have shown the proportion of goitrous people to be as high as 1 in 23 in Sweden, over 1 in 10 in Italy, and 1 in 5 in Mexico. In 1944 in England and Wales, some 500,000 school children and

young adults were estimated to have some thyroid enlargement.

While the most notorious goitrous regions of the world are in the high mountain areas of the Himalaya, Alps, Pyrenees, and Andes, goitre can equally occur in low-lying areas and even in coastal regions. Much work has been done on the relationship between endemic goitre, the geology of the districts in which it is found, and the mineral content of the drinking-water. While this lies outside the scope of the present article, it may be mentioned that some of the most goitrous districts of England are in areas covered by carboniferous limestone, and that the prevalence of goitre in Derbyshire even led to the use of the term 'Derbyshire neck' for the condition.

Although various mineral and other factors may influence the production of goitre in some circumstances, it is now generally accepted that the basic cause of goitre is simply iodine deficiency. As far back as 1500 B.C. the Chinese were using burnt sponge as a remedy for goitre, and the use of sponge and similar natural iodine-rich remedies is found again and again in medical writings. Within a few years of its discovery in 1811, elementary iodine was tried as a remedy for goitre, but owing to adverse effects from excessive doses it was discredited for many years until its recognition as a normal constituent of the thyroid in 1895. Many studies, in which Marine and Kimball in the United States were pioneers, have since demonstrated the efficiency of small amounts of iodine in preventing endemic goitre. The cheapest, safest, and most convenient method of giving it is by the iodization of table salt with sodium or potassium iodide, originally suggested by Boussingault in 1833. The equally efficacious iodate, which is rapidly reduced to iodide in the body, may be used instead, and unlike iodide it is not liable to undergo loss on storage. In a number of countries iodization of table salt is compulsory; though widely practised in Britain and the United States it is not at present obligatory, and in fact objections are sometimes raised against it. However, it is generally believed that the tiny amounts of iodine involved (the maximum addition is one part to 10,000 parts of salt) are absolutely safe.

More serious than deficiency of thyroid hormone in an

adult is deprivation during foetal life and early childhood, since it plays a vital part in mental and physical development. In its absence irreversible damage may be done, so that even treatment with thyroid may do little more than prevent any further deterioration. The condition that results is known as *cretinism*, and though the end result is similar, a number of causes are now recognized. Endemic cretinism, attributed to iodine deficiency, is found in many goitre districts, particularly in children of goitrous mothers. The relationship of cretinism to goitre is not simple; some goitre areas such as those in the Andes are nearly free of cretinism, and cretinism is commoner in goitre districts where there is much intermarriage.

The American goitre authority, Marine, once said 'simple goitre is the easiest and cheapest of all known diseases to prevent' and it can be controlled '. . . by available methods as soon as organized society determines to make the effort'. Perhaps the slow progress in abolishing goitre and its associated diseases is partly due to their somewhat less spectacular nature compared with killer diseases such as cholera and malaria.

Sporadic cretinism can occur in non-goitrous areas, and is the childhood equivalent of myxoedema. It may be due to atrophy or absence of the thyroid gland, or to some more recently recognized metabolic defects in one of the stages leading from inorganic iodide to active hormone, such as an inability to effect the initial oxidation from iodide to iodine. Recently some cretins who showed little response even to thyroid medication have been found to show dramatic improvement with tri-iodothyronine, and in these cases there is believed to be a congenital lack of the enzyme which de-iodinates thyroxine to tri-iodothyronine in the body.

A recent suggestion concerning the nature of a form of hypothyroidism known as *Hashimoto's disease* (lymphadenoid goitre) may have important significance in fields other than thyroid physiology. In this condition symptoms of hypothyroidism accompany an enlarged thyroid, while the blood contains abnormal proteins of the gamma-globulin type. These, it now seems likely, are actually antibodies produced by an immunological

response to a leakage of thyroid protein into the circulation, which then have a destructive effect on the patient's own thyroid gland.

Hyperthyroidism

The reverse picture to myxoedema is seen when an excess of thyroid is fed to an animal, or in humans when an excessive amount of hormone is liberated from the gland, producing symptoms known collectively as thyrotoxicosis. This occurs in Graves' disease, known on the Continent as Basedow's disease. (Graves was a Dublin physician who published observations on the disease in 1835, five years before Basedow did so; however, the condition had already been described as early as 1786 by Parry, a physician of Bath.) The disease is characterized by a marked increase in the basal metabolic rate with nervousness, sweating, and wasting, and if untreated may result in death due to exhaustion of the heart. Varying degrees of thyroid enlargement and protrusion of the eyeballs often occur, hence the alternative name 'exophthalmic goitre' for the condition.

Therapy has been hampered by a lack of knowledge of the origin of the disease, particularly whether it is primarily a disease of the thyroid or not. Treatment is, however, normally directed at the thyroid, and may be very effective.

Surprisingly, iodine may effect a dramatic improvement for a time in cases of primary thyrotoxicosis, that is to say in patients where the condition arises spontaneously, often after an emotional upset or period of strain, as opposed to secondary thyrotoxicosis which affects some previous goitre-bearers. Apart from the use of iodine, surgical removal of part of the thyroid was for long the only method of dealing with the condition, until in the early nineteen-forties when it was discovered that a number of substances had antithyroid activity, i.e., depressed the functioning of the thyroid gland.

Antithyroid drugs

The number of substances shown in the last decade and a half to have varying degrees of antithyroid activity is very large, and

a few of these have been widely used in the treatment of Graves' disease. The doses administered are carefully controlled so that the amounts of thyroid hormone liberated are reduced to normal levels; too great a dosage will, of course, eventually result in myxoedema.

Antithyroid activity was first observed in some of the sulphonamide drugs, but the first compound used clinically, in 1943 by Astwood in America, was thiourea. Large doses of this unpleasant drug were needed, and it was soon replaced by more active and less noxious compounds containing the thiourea nucleus in a six-membered ring, the thiouracils. In addition to thiouracil itself and its methyl and propyl derivatives, widely used drugs in more recent years have been the five-membered ring compounds methimazole and carbimazole (official British pseudonyms – chemical nomenclature of this class is confused).

Thiourea and its derived antithyroid drugs can react in more than one form, one of which contains the mercapto or thiol group, —SH, which is believed to be essential for activity. An apparent exception is carbimazole, the ethoxycarbonyl derivative of the very active methimazole. Carbimazole has some advantages over its parent drug in lower toxicity, lack of taste and longer duration of action, but is presumed to be hydrolysed back to methimazole in the body before showing its antithyroid effect. The drug structures are all illustrated in the thiol form (Figure 3).
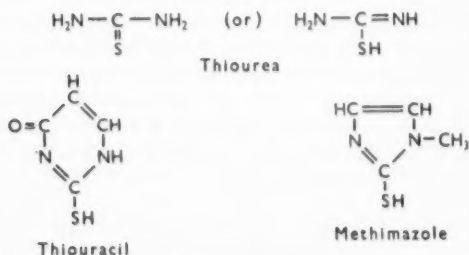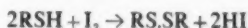

Fig. 3. Antithyroid drugs.

A characteristic reaction of the thiol group is its reaction with elementary iodine, in which two molecules are oxidized to one molecule of a disulphide while the iodine becomes reduced to iodide:

$$2RSH + I_2 \rightarrow RS.SR + 2HI$$

One could imagine the drugs to react in this way with iodine in the thyroid, reconverting the iodine to iodide and so preventing the essential iodination of tyrosine, but the apparent feasibility of this simple reaction does not mean that this is necessarily how the drugs act.

Thiocyanate, e.g., KCNS, once used in the treatment of hypertension, interferes with an earlier stage of thyroid hormone synthesis by preventing the initial iodide uptake and discharging iodide already present in the gland. Potassium perchlorate, $KClO_4$, was more recently shown to behave similarly and has been successfully used in treating Graves' disease.

A wide variety of other substances, not practicable as drugs for various reasons, have nevertheless marked antithyroid activity. A number of cases of myxoedema were traced to this effect of resorcinol (meta-dihydroxybenzene) absorbed over a long period from an ointment applied to leg ulcers.

Naturally occurring goitrogens

In 1928 workers at the Johns Hopkins Medical School in Baltimore had an epidemic of goitre in their rabbits, whose diet consisted mainly of cabbage. Since then, many foodstuffs, mainly of vegetable origin, have been found to possess some antithyroid activity. Interest has centred particularly around the cabbage family (Brassicae), many members of which contain quite high concentrations of a new class of antithyroid substances, the thio-oxazolidines. Most investigated has been 5-vinyl-2-thio-oxazolidine, but the 5:5-dimethyl and other analogues are also known (Figure 4).

The highest concentrations are usually found in the seeds, though not as it happens in mustard seeds, the only ones commonly eaten by man. The most goitrogenic food in this class appears to be the swede (rutabaga in America), but these and

D

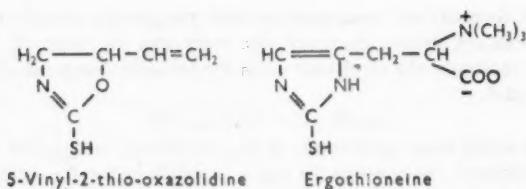5-Vinyl-2-thio-oxazolidine   Ergothioneine

Fig. 4.

similar vegetables do not seem likely to involve any goitre risk in humans; not only are the goitrogens lost in normal cooking, but owing to rapid excretion and metabolism they would only show an effect if eaten frequently and continuously. The risk is greater with farm animals due to their less varied diet.

Under abnormal conditions the goitrogenic nature of some human foods may become more important, and claims have been made (and denied) that some wartime goitre was attributable to greater amounts of brassicas eaten when food was in short supply. In the last few years it has been reported that iodide administration has not succeeded in abolishing goitre from some parts of Australia, Tasmania, and New Zealand. There is evidence that this is due to a goitrogen in the milk from cows fed on marrow-stem kale, or which graze on pastures contaminated with some types of weed. Calves from these cows show marked thyroid hyperplasia.

Occasionally two races living in the same district have been observed to show different incidences of goitre. This has usually been attributed to differences in the iodine contents of their diets. However, in some parts of Fiji where Indians and Fijians live in close association there is noticeably more goitre among the Indians than among the Fijians, and since fish often features in the Indians' menus the presence of a natural goitrogen in their diet was suspected. One of the more obvious dietary differences between the two races is the large consumption of curried foods by the Indians, and in 1951 the author was asked to see if the locally used curry powder contained any antithyroid

activity. Results by a number of methods were quite negative, but the interesting incidental observation was made that experimental rats relished a diet containing 10 per cent of curry powder, and grew much better than th᾽ animals on the same diet but without the curry!

Ergothioneine

This strange substance (see Figure 4) occurs in such varied sources as the fungus ergot of rye, porage oats, animal red blood corpuscles and, in high concentration, in the seminal plasma of the boar. It is mentioned here as it is the only mercapto-imidazole known to occur naturally. Despite its structural similarity to some of the most active antithyroid drugs, however, ergothioneine appears to be without effect on the thyroid gland. Its function, if any, is unknown. It has been suggested that it protects the thiol groups of, for example, cysteine, against various inactivators, and recent American work indicates a possible function of ergothioneine as a constituent of an enzyme system.

RADIO-ACTIVE IODINE

An article attempting to cover, however briefly, the field of thyroid chemistry would be incomplete without some mention of the part played by radioactive iodine both in research and in the diagnosis and treatment of thyroid disease.

The atomic weight of natural non-radioactive iodine is 127, and that of the active isotope almost entirely employed is 131. The latter has a half-life of eight days, and emits β- and γ-radiation. It has a longer history of research use than most radioactive isotopes, since, before it was available from atomic reactors, small amounts had been prepared by bombardment of tellurium with α-particles in a cyclotron.

After administration by mouth or by injection, ^{131}I behaves exactly like ^{127}I but can, of course, be detected and measured by its radiation. Some of the dose becomes incorporated into the various iodine-containing amino-acids, which can then be separated chromatographically. Paper chromatography is used for small quantities, the positions of the radioactive amino-

acids being found by making a photographic record (auto-radiography). On a larger scale, separations are effected by column chromatography, when Geiger counters show the presence of the different fractions in the outflowing solvent. It is difficult to imagine the discovery of tri-iodothyronine and subsequent developments taking place in the absence of these combined techniques.

Large numbers of potential antithyroid drugs have been examined in the first instance by finding out how they affect the rate at which a rat's thyroid picks up an injected dose of radio-iodine. Further, by means of a counter placed over the neck of a human subject, the antithyroid activity of a compound may be estimated in man directly. Briefly, the technique consists of giving a tracer dose of radio-iodine, and measuring the isotope as it becomes fixed in the thyroid. When a steady straight-line graph of the counts per minute plotted against the square root of the time in minutes since administration has been obtained, the drug under test is given and the readings continued. The amount by which the graph is deflected from its original line towards the horizontal is a measure of the activity of the compound in man (Figure 5).
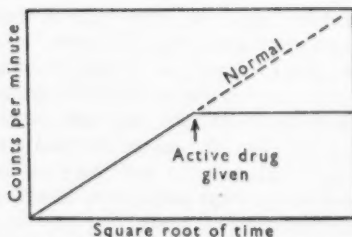

Fig. 5. Measuring the activity of antithyroid drugs with radio-iodine.

When a diagnosis of hypo- or hyper-thyroidism is in doubt, much valuable information may be gained from the rate of thyroidal uptake or of urinary excretion following a tracer dose of radio-iodine. Prior to an operation, the exact position of an

enlarged thyroid, or of a growth which similarly concentrates iodine, may be found by externally plotting contours of radio-activity (Figure 6).
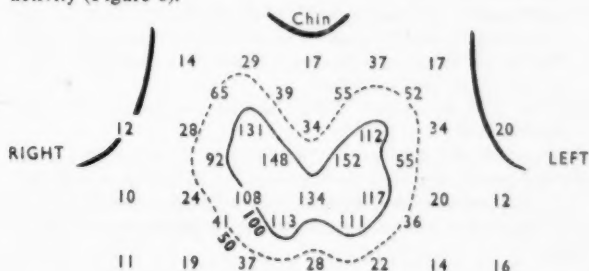

Fig. 6. Distribution of a tracer quantity of ^{131}I in the thyroid gland as shown by the counting rates of a directional Geiger counter placed over the neck. (*Courtesy of Prof. F. W. Speirs, University of Leeds, and the Royal Institute of Chemistry.*)

Considerably larger doses of radio-iodine are used therapeutically in cases of hyperthyroidism and of thyroid cancer. Some such cancers, and their metastases in other parts of the body, concentrate iodine much like normal thyroid tissue; they thus also concentrate radio-iodine, which can effect their selective destruction wherever they may be situated.

Similarly a carefully calculated dose of radio-iodine can be employed to destroy part of the thyroid's function in cases of hyperthyroidism. Despite its apparent simplicity the method has not been widely used in this country, partly owing to the fear of damaging other parts of the body and of malignant changes being initiated. While these risks are believed not to be large, the method is usually reserved for special cases.

FURTHER READING

Harington, C. R.: *The Thyroid Gland: its Chemistry and Physiology.* (Oxford University Press, 1933.)
Pitt-Rivers, R., and Tata, J. R.: *The Thyroid Gland.* (London, Pergamon Press, 1959.) (In the press.)

Iodine Facts: World Goitre Survey. (London, Chilean Iodine Educational Bureau, 1946.) Summarizes more thyroid information than is indicated in the title.

'Endemic Goitre,' *Bulletin of the World Health Organization*, Geneva, 1958, Vol. 18, Nos. 1–2 includes an exhaustive article on the world distribution of goitre, with shorter papers on iodine metabolism, goitre therapy, and iodized salt.

Lenihan, J. M. A.: *Atomic Energy and its Applications*. (London, Pitman, 1954.)

More technical articles on subjects such as the antithyroid drugs, ergothioneine, etc., may be found in review journals, e.g., the 'Annual Reports' of the Chemical Society, London, and the American *Annual Review of Biochemistry* and *Annual Review of Physiology*.

RESEARCH REPORT

A. W. HASLETT

DISCOVERIES FROM SATELLITES

THE most interesting, because unexpected, result of observa-
tions made from satellites up to the present time has been the
discovery of a region surrounding the earth where there are
between 1,000 and 10,000 times as many charged nuclear par-
ticles as had been expected from cosmic ray observations at
lower levels. The existence of this region was brought to light
by Professor J. van Allen of the State University of Iowa by
instruments included in the Explorer satellites. As a speaker at
the recent Royal Society of London discussion on space re-
search put it, 'He was at hand with an instrument that worked; it
was as simple as that' – a rather strong argument for paying as
much attention to preparing instruments as satellites.

The region of high particle density begins at about 600 miles
altitude and extends to a distance from the Earth that has yet to
be determined. If observations made with the lunar probe
(Pioneer) can be trusted, the region is of limited extent. Recep-
tion of telemetered observations from Pioneer did not begin
soon enough to overlap with those from the Explorer satellites;
but when they did begin, the particle density recorded was low.
In terms of latitude, the Explorer observations suggested that
there was a peak density of particles above the Equator, with
further peaks to the north and south, probably in about the same
latitudes as those in which displays of aurora are most frequently
observed.

Professor van Allen attributes the region of high particle
density to the trapping of incoming particles by the magnetic
field of the Earth. This explanation was supported at the Royal
Society discussion by Professor T. Gold, who argued further

that after remaining for an average of about a month in the trapping region the trapped particles might be expected to leak towards the Earth. The trapped particles are thought to come mostly from the Sun. Their direction of first arrival would be disguised at lower levels by their stay in the trapping region, and they probably account for many of the lower-energy particles described loosely as cosmic radiation. Higher-energy particles, on the other hand, would come straight through without being trapped. It is these that are of interest in nuclear physics, and previous evidence still stands that they come mostly from outside the solar system, possibly even from outside the Galaxy.

Also of interest is the association between particles from the trapping region and aurorae. While a general connexion between aurorae and solar activity has been established for some long time, and many individual solar flares are followed by increased displays, the connexion does not work out in detail. An explanation of this is now provided. If a high proportion of the particles emitted by the Sun are held up temporarily in the trapping region, then a detailed, day-to-day correlation between aurora and events on the Sun is not to be expected. There are clearly many questions that only more observations can answer. Among them are the extent of the trapping region; the distribution in number, energy, and direction of incoming particles beyond it; the energy limits of the trapped particles; and their variation in number and energy with the solar cycle. Pioneer 3 may have answered the first of these questions. There remains in the rest a case for more satellites and space probes.

In another instance, observations made from satellites have differed sufficiently in quantity from those made previously to raise new problems. Whereas previously physicists have been required to account for temperature gradients in the upper atmosphere of the order of five degrees centigrade per kilometre, it appears that gradients as high as twenty or even thirty-five degrees per kilometre must now be accounted for. To Professor S. Chapman, the big inwards flux of energy which this implies is evidence for his theory that the hot corona surrounding the Sun extends, in effect, to the Earth. The peak temperature

in the corona is probably about 1,000,000 degrees absolute. From estimates of the thermal conductivity of a hot, diffuse gas, Chapman concluded that the temperature even at the distance of the Earth might be more than 200,000 degrees. Professor D. R. Bates, of Belfast, was not convinced that any special new theory was needed.

Measurements of electron density in the upper atmosphere, made from the Russian sputniks, have neatly rounded the region of maximum electron density, which had been approached but not quite reached in rocket measurements. The maximum is at rather more than 300 miles altitude. The sputniks have covered the beginning of the falling off, but beyond this there is at present a long gap until distances of the order of a few thousands of miles from the Earth. Here tentative information is given by the 'whistler' type of atmospheric, which travels from one hemisphere of the earth to the other and sometimes back again, passing through very high regions of the atmosphere on its journey.* Many 'whistler' recordings have been made as part of the I.G.Y. programme, and the accuracy of the conclusions drawn from them may be tested directly at any time.

A further point of interest is the practicability of drawing more accurate conclusions about the shape of the Earth than has been possible from observations made at ground level by the methods of geodetic survey. This had been mentioned as a possibility from the beginning, given sufficiently accurate observations of the path followed by satellites. But to disentangle the effects produced by air drag and by gravity – through the departure of the Earth from an exactly spherical shape – had seemed likely in advance to require more accurate observations than could reasonably be hoped for. In the event, the Royal Aircraft Establishment, Farnborough, has done exceptionally good work on the sputnik orbits; and, following a suggestion made by Professor E. Buchar from Prague, the problem has been shown to be less intractable than it first looked. As pointed out by R. H. Merson and D. G. King-Hele, of Farnborough, the first-order

* See, for example, *Science News*, **29** 104.

effects of air drag and the shape of the Earth are of different kinds. That of air drag is to lower the high point (apogee) of a satellite's orbit and to make the orbit less elliptical. A first-order effect of the bulging of the Earth at the equator is to cause the plane of the satellite's orbit to rotate about the axis of the Earth. Therefore, to a first approximation, the effects can be separated. Using the rotation of the orbital plane of Sputnik 2 as their main data – with data from Explorer 1 providing a check on interpretation – Merson and King-Hele have concluded that the Earth is slightly less flattened at the poles than had been thought by geodesists. On this evidence, the distance from North to South Pole through the centre of the Earth is about 160 yards longer than it was thought to be. But there remains a loophole for argument; and the substantial claim now advanced is that, with more satellites to work on, the accuracy attainable should be about ten times as great as can be got from geodetic surveys.

The main purpose of the two-day discussion held by the Royal Society was to direct attention to the fact that too little thought has been given to experiments that might be done with satellites and space probes, and the equipment needed to do them, compared with the problems of launching and placing in orbit.

Buchar, E.: *Nature*, 1958 **182** 198.
Merson, R. H., and King-Hele, D. G.: *Nature*, 1958 **182** 640.

MAN-MADE 'AURORA'

On any view of the evidence, there is much of interest in reports, assembled from Apia, Samoa, and published from New Zealand, of the occurrence of magnetic disturbances, interruptions of radio communications, and the appearance of striking chromatic effects in the night sky – all as common sequels to a high-altitude nuclear explosion 2,000 miles or so to the north, on the opposite side of the equator, on 1 August 1958.

Information about the explosion is meagre. According to an official announcement at the time, a nuclear warhead was exploded at a high level above the Pacific proving grounds. According to newspaper reports, the explosion took place at a

height of 100 miles above Johnston Island, and the light from it was clearly visible throughout the Hawaiian Islands, which means at distances approaching 1,000 miles. If the latter statement is taken to imply a direct view of the flash, the height would have been at least 115 miles. Merely from the scale of the effects, it must have been a thermonuclear explosion. The temperature reached would, in that case, have been of the order of some thousands of millions of degrees. But for comparison with effects observed in Samoa, neither the height at which the explosion took place, nor the energy released, nor the temperature reached can be more than roughly estimated or guessed. Also, it is not known which are the predominant nuclear reactions in current thermonuclear explosions. Some conclusions of a more practical kind can, however, be drawn. Among them are the following: a thermonuclear explosion was effected in a rocket warhead; radio communications were affected 2,000 miles away; the explosion, although at a high altitude, could have been detected at a distance of at least 2,000, and probably 3,000, miles.

The effects in Samoa were reported in the first instance by J. G. Keys, observer-in-charge at Apia Observatory, and in the form of a letter to *Nature* by A. L. Cullington, of the Geophysics Division, the Department of Scientific and Industrial Research, New Zealand. The suggested connexion between events in Samoa and the explosion depends in part on timing and in part on the unusual character of the events. The earliest recorded time for the onset of magnetic disturbance was 1050 G.M.T. The explosion is said to have taken place approximately at the same time; more exact information is presumably lacking, although there seems to be no good reason for silence on this point. Effects described as 'a man-made aurora' were first observed one minute later. Radio fade-outs are said to have been associated with the 'auroral' display and to have lasted from one to several hours. Details of affected frequencies and times have not been given.

The next part of the argument is that the events reported were exceptional. The records of magnetic disturbance at Apia

were sent to New Zealand for examination, and are described by Cullington as unusual compared with other records at Apia. The 'sudden commencement' of the disturbance was of a type seldom observed there, and was about four times as big as is usual for this form of commencement. Yet the disturbance was not world-wide, but appeared to be localized in the Central Pacific. The visual effects also seem to have been unusual, no matter in what way they are interpreted.

The display began with bright rays in the western sky, at first violet covered with reds, then changing gradually to greens. There was also a crimson arc to the north with its centre 32 degrees above the horizon, and three or four red bands, with their centres roughly due south and at elevations of about 30 to 40 degrees. The display was first taken to be aurora australis (australis because Apia is on the south side of the equator). If so, it would have been so completely unusual as virtually to exclude an explanation on these lines. Only one previous case of aurora has been reported from Apia, and that as long ago as 1921. Second, all reports of aurora seen anywhere in the tropics have been at times of world-wide magnetic storms, and the displays have been at low angles to the north or south.

Those who collect reports of aurorae are accustomed to reports in which the effects described are found on inquiry to be attributable to light scattered in the atmosphere. But the local time was 11.15 p.m. to about 11.30 p.m., so scattered sunlight is excluded. Moreover, the displays to the north and south suggest an effect analogous to aurora; and the form of the magnetic 'sudden commencement' is described as 'similar to that which one would expect at a high-latitude station near the auroral zone'.

In Cullington's summary, 'there seems to be little doubt that the unusual magnetic effects recorded at Apia are related to the explosion and that the manifestation seen at Apia was a man-made or artificial aurora due to a nuclear explosion in the upper atmosphere. A study of the effects due to this explosion may throw considerable light on the theory of magnetic storms and aurorae.' According to later newspaper reports, a number of

photographs were taken. These, if good enough, should provide a check on the conviction of Keys – and, at second hand, of Cullington – that the visual effects were essentially of the same kind as natural aurora. Viewed at third hand from England, the coincidence of explosion and regional magnetic disturbances, radio fade-outs, and visual effects appears too remarkable to be attributed to chance. The identification of the visual effects with a form of aurora is less well supported by evidence, although they appear difficult to account for otherwise. Should a further high-level explosion be undertaken from Johnston Island, it would be helpful if advance notice could be given to Apia. But to arrive at anything that could be described as a theory of the effects, it would be necessary to have more information about the explosion as such than is likely to be given. As well as height, energy release, and temperature, it would be important to know also whether fission or fusion reactions provided the main source of energy.

Cullington, A. L.: *Nature*, 1958 **182** 1365.

ECHOLOCATION BY WHALES

Bats having been shown already to make use of a highly developed system of echolocation to catch insects, at least two species of toothed whales are now strong candidates for the use of a similar system to catch fish and avoid obstacles. Trains of pulses, extending into ultrasonic frequencies have been recorded in captivity from one of the smaller species, the bottle-nosed dolphin (*Tarsiops truncatus*), commonly described as a porpoise, and also under natural conditions at sea from the sperm whale (*Physetor catedon*). The recordings of sounds made under water by the bottle-nosed dolphin were made by Professor W. N. Kellogg and his colleagues of Florida State University, and published in 1953. Those from the much larger sperm whale were made with the ordinary echosounding equipment of the research vessel *Atlantis* of the Woods Hole Oceanographic Institution, Massachusetts, and reported by E. L. Worthington and W. E. Schevill in 1957. Evidence suggesting the use of echolocation by

one species may thus be taken not unreasonably as suggesting its use also by others. Evidence which comes close to proof in the case of the bottle-nosed dolphin has been published lately by Professor Kellogg.

His experiments were done on a pair of animals given to the Marine Studios of Marineland, Florida, and transported 260 miles by road to the university's laboratories. They were kept in a mud-bottomed dredged pool, connected by concrete pipes to a seawater creek. The tidal range was only 1·5 ft, and the fact that Gulf coastal water is naturally brownish in summer was also a help in experiments. Together with the stirring up of mud by the porpoises, visibility was limited to a maximum of between 10 and 20 inches; and the possibility that vision might be used was more easily excluded. Use of a sense of smell was treated as impossible; the bottle-nosed dolphin has no olfactory bulb, and keeps its nose or blow-hole closed while under water. Its sense of hearing, on the other hand, was known to be acute and to extend at least two octaves above the highest frequencies heard by man. From the sound-recording experiments already mentioned, underwater noises made by the animal were known to include trains of short pulses, with individual pulses as short as one millisecond, and including a range of ultrasonic frequencies.

In the first and simplest series of experiments, a variety of objects – including dead fish, which were an accustomed food, and streamlined shapes which could be lowered into the water without detectable noise – were introduced into the pool. The response to noisy introductions was usually a torrent of sputtering pulses. As the target was approached, the bursts became continuous, and the animal moved its head slightly from side to side, as if to get a better indication of direction. Afterwards, occasional, apparently exploratory, bursts of pulses were resumed. When an object was introduced without making a noise, there was usually an interval, which might be 10 or 15 seconds, before the porpoise responded – apparently after an exploratory burst had been emitted. After the first burst, there came a stream of them. If an identical object was introduced with a splash, there was no interval.

Other tests were of ability to avoid obstacles. Triangular metal posts, with sides 2 inches long, and spaced 8 feet apart, were arranged so as to give a rectangular pattern of obstacles. There were six rows, each containing six posts; and touches with the posts were recorded electrically. The porpoises made some touches at first – apparently with their sides when turning. But after a few trials, they learnt to make no touches at all, even on moonless nights.

The female porpoise was the older, and also was less inclined to co-operate. So, in the next series of experiments – designed as a test of discrimination – only the male porpoise was used. He was trained to discriminate between a small fish, about 6 inches long, which he liked, and a larger fish, about 12 inches, which he had once liked but got tired of. In a final series of 140 trials – some in almost total darkness – he made no mistakes. As a general comment, Professor Kellogg points out that the speed of the animals' response was too great for an explanation in terms of taste: 'The response is like that of a dog picking up a stick on the run.'

There were still two further series of experiments. In one of them, fish of the preferred kind were presented simultaneously in box-like containers, one with an open side, giving free access, and the other with entry barred by a glass window. Even the co-operative male porpoise was at first hesitant to put his head into the open box; and, when this had been overcome, the experiment took a different turn from that expected. What happened was that the porpoise learnt to position himself in advance before the opening that was not blocked by glass – presumably detecting the glass by echolocation.

This was tested by Professor Kellogg. In a final series of experiments, he divided the pool into two sections by a steel mesh fence, leaving two openings, one or other of which was blocked by transparent plastic. The porpoises were then chivvied from one section of the pool to the other. Each was given 50 trials, and they made, between them, only two mistakes out of 100. In all the experiments, under-water signals were recorded, and 'the conclusion seems inescapable that the porpoises

avoided the solid but invisible door by means of echo ranging'

Kellogg, W. N., Kohler, R., and Morris, H. N.: *Science*, 1953 **117** 239.

Worthington, E. B., and Schevill, W. E.: *Nature*, 1957 **180** 291.

Kellogg, W. N.: *Science*, 1958 **128** 982.

SHIP HYDRODYNAMICS

A new National Ship Hydrodynamics Laboratory is due to begin operation at Feltham, Middlesex, before the end of the present year. The equipment which most impresses the eye is a 1,300-ft tank in which model ships can be towed from a carriage, and waves of up to two feet in height generated. The most attractive for spectators will be a basin, 100 ft by 100 ft, in which remotely controlled models can be directed at any desired angle to the waves generated, and real-sea conditions can be reproduced. In comparison with other laboratories, the outstanding piece of equipment is a water tunnel for the study of cavitation in propellers – the formation of bubbles of water vapour or air in regions of low pressure, whose subsequent collapse leads to vibration and, in extreme cases, to loss of power. Since the bubbles must be reabsorbed, it is necessary to design a circuit in which there is substantial variation in pressure. This leads to a vertical form of circuit. In the design used at Feltham, the lower or return limb is 180 ft below ground level. With this water tunnel it will be possible to test model propellers of up to 22 inches diameter, at speeds of up to 30 knots. The size is big enough to lead to reliable predictions of full-scale performance at the same speed, with extrapolation up to about 60 knots. This tunnel is the biggest of its kind yet built.

SOME BOOKS RECEIVED

THE UNIVERSE – A Scientific American Book (London, Bell and Sons, 1958), pp. 142, 13s 6d.

This is yet another collection of articles reprinted from the *Scientific American*. They cover the history of cosmological thought, the substance and the form of the Universe, cosmological theory, etc. Three of the articles are by distinguished English thinkers, Fred Hoyle and Martin Ryle of Cambridge, and Professor Herbert Dingle, who supplies a cautionary envoy urging cosmologists to keep their speculations and guesses within the framework of accepted scientific method.

Included is a section on the Universe in photographs – some twenty plates of unimaginably remote parts of the Universe as revealed by the 200-inch reflector on Palomar Mountain.

SCIENCE IN SCHOOLS, edited for the British Association for the Advancement of Science by W. H. Perkins (London, Butterworth's Scientific Publications, 1958), pp. 150, 15s.

If, for reasons of national prestige, Britain is foolish enough to be persuaded to engage in the current lunar rocket race, we are in for a decade of aiming at the moon without much hope of hitting any worthwhile stars. If our resources were limitless such lunacy might not matter, but how can we equate the dissipation of a million or so pounds at every step in this mad race with the fact that the expenditure on equipment to teach science even in a maintained boys' grammar school may be as low as 1s 1d. per pupil per year. True this represents the minimum, but what of the twenty-six girls' schools with between 1s 3d. and 3s 6d.

These are but a few of the disturbing facts revealed in this useful account of the Conference arranged by the British Association in the Spring of 1958. Other facts that come to light are, for example, that tens of thousands of our young people are being deprived of all formal contact with scientific teaching because there is simply no one to teach them.

After reading this important publication it is difficult to understand how anyone can fail to see that raising the standard of scientific

learning in the population as a whole must come before the luxury of prestige satellites.

THE UPPER ATMOSPHERE by H. S. W. Massey and R. L. F. Boyd (London, Hutchinson, 1958), pp. 333, 63s.

Although not bound by the equivalent of a Hippocratic oath, for many generations scientists regarded themselves as belonging to an international brotherhood. The twentieth century has witnessed a sad decline in this attitude, and the harnessing of science to national rather than humanitarian ends. But despite this, during the International Geophysical Year, scientists of the world are again at this very moment collaborating to an extent far exceeding that of any other human group.

In this volume Professor Massey and Dr Boyd present an authoritative account (largely without the aid of advanced mathematics) of the researches on the upper atmosphere that are being undertaken during the I.G.Y. The phenomena discussed in detail include radio fadeout, radio absorption, night airglow, aurorae, meteors, cosmic rays, magnetic effects, and so on.

The volume is designed for students and those scientists in other fields who require a reliable outline of the subject. It is illustrated by a large number of line drawings and photographs, some of which are in colour. There is a short general bibliography and an adequate index.

MIND AND MATTER by E. Schrödinger (Cambridge, at the University Press, 1958), pp. 104, 13s 6d.

Ever since man became a thinking being, the duality of mind and matter has presented a puzzle to philosophers and scientists alike.

In this little volume – which is based on the Tarner Lectures that he gave in Cambridge in 1956 – Professor Schrödinger analyses some of the paradoxes arising from this dichotomy, and offers his own suggestions for a solution of the problem.

THE ECOLOGY OF INVASIONS BY ANIMALS AND PLANTS by Charles S. Elton (London, Methuen, 1958), pp. 181, 30s.

At the end of the war the reviewer bought a house with a garden bordered by an open plantation of Austrian pine. Wartime years of

occupation with other more vital matters had led to the 'neglect' of the plantation. Birches and oaks had seeded themselves: pleasant grassy paths meandered through breaks of wild rose, bramble, and hawthorn ten feet high. Countless birds nested in the thickets: each spring the cuckoo visited the plantation in search of foster parents for its foundling eggs.

Then an efficient local authority thought that it was time to clear the place up. They went through it with fire and pruning hook. The undergrowth was razed to the ground and burned: the lower branches of the pines were lopped. When all was finished, the wood was a model of official tidiness – you could see from end to end of it, and the fresh cold wind swept its length. But the cuckoos never came again. They've been replaced by a pair of wood pigeons who use the lengthening trees to spy on the adjacent gardens: cow parsnip has invaded all the clearings: the lads and lasses go somewhere else. This is ecology.

In this rather young science, which is concerned with plant and animal populations, their balance, and the changes in them, Charles Elton is a pioneer. In this volume, which is an expansion of a group of talks he gave on the B.B.C. Third Programme, he distils the wisdom acquired through many years' study. Over a hundred illustrations in line and half-tone add greatly to its value. Each chapter is fully documented and there is a full index. Coming from one who had done so much to build up the present more enlightened understanding of conservation problems this volume cannot fail to take an important place in the story of man's relation to nature.

MAN'S EMERGING MIND – Man's progress through time – trees, ice, flood, atoms, and the Universe, by N. J. Berrill (London, Dennis Dobson, 1958), pp. 308, 21s.

The scope of this volume is somewhat wider than its title might at first suggest, in that it contains a valuable background of palaeontological and zoological material.

The author is a Bristolian who is now Strathcona Professor of Zoology at McGill University, Montreal, Canada, and every page is marked by the evidence of an uncommonly well-furnished mind. Indeed, few books in recent years have, in the reviewer's experience, presented such a well-balanced account of man as the supreme (for the present) inhabitant of our planet. Nor is the author unaware of

the dangers that lie ahead, if man is to retain the position in which
nature has placed him.

'We can always be wise in hindsight but I am convinced we will
never foresee the full consequences of any action we may be
inclined to take. Therefore we have to retain intelligence and
adaptability and play along always with a minimum of interfer-
ence with the scheme of things. As an incorporated part of nature
we can live wonderfully within her, but as a self-ejected outcast
turning to fence with the living earth, we are outmatched from the
start. I am speaking neither in parables nor similes. This earth
is a living planet, although it is alive in ways that we do not
fully comprehend, and unless we conform to the rules of life we
are in danger both from within and without. When efficiency is
less a fetish, when to live signifies more than getting from here to
there, when idleness is no longer boredom but opportunity, when
there is time for listening, when cornflowers and poppies belong
in the wheat, only then will we know that we are re-entering our
heritage.'

Here, indeed, is the greatest story of all time told with disciplined
imagination.

PATTERNS OF DISCOVERY – An inquiry into the conceptual
foundations of science by N. R. Hanson (Cambridge, at the
University Press, 1958), pp. 241, 30s.

Dr Hanson is a Fellow of St John's College, Cambridge, and Pro-
fessor of Philosophy at Indiana University. In this essay he contends
that, while elementary particle theory has been much discussed by
philosophers of science, its features have not in fact been properly
understood by them, and it is to examine this misrepresentation of
microphysics by philosophers that he has written his essay.

It is directed at both philosophers and scientists. From it the latter
will derive a new understanding of the philosophical and historical
background of their researches; the former now have a fresh account
of the nature of scientific discovery.

The work is divided into six sections: observation, facts, caus-
ality, theories, classical particle physics, elementary particle physics,
and nearly a third of the volume is taken up by explanatory notes on
these major sections. No one need assume that this is an easy book,
but Dr Hanson's familiarity with both science and philosophy
creates a work worth assimilating in small doses.

EVERYDAY METEOROLOGY by A. Austin Miller and M. Parry (London, Hutchinson, 1958), pp. 270, 30s.

If it were not for its intrinsic complexity, there would be no more useful entry into science than through an understanding of the weather, because, apart from supplying a topic of conversation in an otherwise publicly inarticulate nation, in a region situated as is Britain in relation to the movement of the great air masses, changing weather has an almost hourly influence on much human activity: farmer, market-gardener, shepherd, fisherman, mountaineer and sportsman, captain of ship and aircraft, even the umbrella-carrying 'city-man' who may be caught unprepared between home and office 'an indignity that he might have escaped had he added wisdom to caution and learnt a little meteorology'.

To augment such native prudence the authors have produced a useful and at times entertaining 'Met without Maths'. It will not transform the amateur weather watcher into a skilled forecaster, but it will increase his understanding and appreciation of a much-maligned government service. And on the score of the forecasts on the inevitable occasions when they go wrong, it is well to remember that:

'The answer may well be that we, the public, get the forecasting service we deserve, or are willing to put up with or, in the long run, are prepared to pay for. By maintaining the Meteorological Office on an annual budget of little more than the cost of a single modern bomber, we are perhaps attempting to get our weather service on the cheap.'

ABOUT OUR CONTRIBUTORS

A. M. P. BROOKES was educated at Westminster and St John's College, Cambridge, where he is now a Fellow. He is a lecturer in the Department of Engineering, Cambridge University, and does research on the impact strength of metals. He is also interested in methods of instrumentation and fine measurement.

A. B. CALDER, a graduate of St Andrews and Edinburgh Universities, is Senior Lecturer in Inorganic Chemistry at the Rutherford College of Technology, Newcastle upon Tyne. F.R.I.C. From 1947 to 1956 he was in charge of the Spectrographic Unit in the Edinburgh and East of Scotland College of Agriculture, where he dealt with the use of spectrographic equipment both for research and advisory purposes in agriculture. He has undertaken a special study of the normal variation in the trace-element content of soils and herbage species with a view to devising a sampling technique suitable for advisory purposes, and for a survey of soils and upland grazing in the East of Scotland area.

D. J. FISHLOCK was educated at the City of Bath Boys' School and the Bristol College of Technology. He spent seven years with the Westinghouse Brake and Signal Co. Ltd, as assistant to the Works Metal Finishing Chemist on control and development work connected with plating, finishing, and corrosion. Conscripted in 1955 he passed an undistinguished military career mainly in Hong Kong, ostensibly maintaining electronic computers in the R.E.M.E. while contributing some 80,000 words to technical journals to supplement his service pay: while abroad he also wrote a book on metal colouring, to be published shortly. Unmarried, and aged twenty-six, he now practices as a freelance technical writer. His leisure interests include humorous literature, the theatre, rugby, and high-gravity ales.

K. MENDELSSOHN, who is Reader in Physics at Oxford, was educated at Berlin University. After holding research appointments there and at Breslau University, he came to Oxford where, early in 1933, he set up at the Clarendon Laboratory the first helium liquefaction plant in England. His work has been mainly concerned with investigations at low temperatures, and particularly with the properties of liquid helium and superconductors. Dr Mendelssohn is a Fellow of the Royal Society, and Vice-President of the Physical Society.

B. D. POWELL was born in 1926 and is a Senior Scholar, and graduate in Natural Sciences, of Trinity College, Cambridge. He has carried out research work in the Department of Colloid Science, Cambridge, and at the N.S.W. University of Technology, Australia. After a period in the Division of Applied Chemistry, National Research Council of Canada, at Ottawa, he returned to England and joined the staff of Cadbury Brothers Limited. Dr Powell's work has included the study of cacao fermentation and drying, in the laboratory and in the field, and he has travelled extensively in the cacao-growing areas of Ghana, Nigeria, and the British Cameroons.

C. E. SEARLE was educated at St Dunstan's College, London, and University College, graduating in Chemistry in 1942. After a period in industry he carried out research at Battersea Polytechnic, leading to a Ph.D. in 1949, and then worked, mainly in the thyroid field, at the Medical Schools of University College Hospital and the Royal Free Hospital. F.R.I.C. Since 1956 he has been engaged in cancer research in the University of Birmingham.

SCIENCE NEWS

EDITED BY ARCHIE AND NAN CLOW

CONTENTS

Front cover: Cocoa pod split open with a cutlass ▶